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U. E. S. DUPLICATE

THE THEORY

OF THE

LEAD ACCUMULATOR

(STORAGE BATTERY).

BY

DR. FRIEDRICH DOLEZALEK.

TRANSLATED FROM THE GERMAN WITH THE SANCTION OF THE AUTHOR

BY

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ROBERT DRUMMOND, PRINTER, NEW YORK.

DEDICATED

TO MY HONORED TEACHER

Professor Dr. W. Nernst

AS A TOKEN OF ESTEEM

BY THE AUTHOR.

TRANSLATOR'S PREFACE.

THE scientific and practical importance of the subject, and the lack of a similar monograph accessible to English-reading students, are sufficiently good reasons for undertaking the labor of a translation.

It affords me great pleasure to acknowledge at this place my indebtedness in the reading of proof to Miss Alice Ankeney and Mr. Harvey H. Lochridge.

CARL L. VON ENDE.

AUTHOR'S PREFACE.

WITHIN the last ten years, as a result of the gigantic development of the lead-accumulator industry, a great number of works have arisen, a part of which treat the lead accumulator only briefly, and a part exhaustively.

Those who wish to inform themselves as to the fundamental laws governing the action of this most important electrochemical apparatus, as well as to the setting up and handling of small batteries, are referred to the small and clearly written work of Prof. Elbs, "Die Accumulatoren."

In the excellent book of Prof. Heim, "Die Accumulatoren für stationäre elektrische Beleuchtungsanlagen," the subject is treated more from the technical standpoint. This work contains, besides a discussion of the most important accumulator types, a detailed account of the systems of arrangement and apparatus necessary to their operation, as well as the estimating of the price of installations.

The same is true of the small work of Gruenwald, which condenses into a small compass much that

APR 10 1922

is worth knowing, including also directions for the manufacture of storage-cells.

Written for the special expert we have the well-known, comprehensive works of Schoop, "Handbuch der elektrischen Accumulatoren" (Stuttgart, 1898), and Hoppe, "Die Accumulatoren für Elektrizität" (Berlin, 1898). The first gives, in addition to a detailed description of nearly all known storage-battery systems, a minute account of the methods of manufacture, while the work of Prof. Hoppe is marked by the fact that all the scientific investigations upon the lead accumulator, as well as the galvanic element, have been taken up in it.

In the works considered above, however, no attempt is as yet made to treat the reactions in the lead accumulator altogether from the standpoint of the new theories of physical chemistry; in fact the assertion is frequently made that these have been fruitless as far as the lead accumulator is concerned.

The following pages are then a first, although possibly a somewhat imperfect, attempt in this direction; they show, however, that the newer theories have found a more exact application in the case of the lead accumulator than in probably any other instance, and have been of a fruitfulness unprecedented. Since the numerous investigagations at hand have made possible the numerical application of almost the entire field of the newer electrochemistry, and have lead to a concise presentation of the subject of the accumulator, as well

as the explanation of the changes in the secondary element, this little work will be of interest to the students of electrochemistry. For the more detailed information as regards the laws upon which the discussions, calculations, etc., are based, the well known works on physical and theoretical chemistry of van't Hoff, Nernst, and Ostwald, as well as the more special manuals of electrochemistry of Jahn, Le Blanc, Haber, Loeb, and Luepke, are referred to.

I gladly take this opportunity heartily to thank Dr. Glaser, Dr. Polzenius, and Dr. von Steinwehr for the reading of proofs and the many suggestions.

F. DOLEZALEK.

GOETTINGEN, Sept. 1900.

CONTENTS.

		PAGE
	PREFACE	v
I.	CHEMICAL THEORY OF ORIGIN OF CURRENT	1
II.	THERMODYNAMICAL THEORY OF ORIGIN OF CURRENT	25
III.	OSMOTIC THEORY OF ORIGIN OF CURRENT	36
IV.	VARIATION OF ELECTROMOTIVE FORCE WITH ACID CONCENTRATION	52
V.	VARIATION OF ELECTRODE POTENTIAL WITH ACID CONCENTRATION	75
VI.	TEMPERATURE COEFFICIENT	93
VII.	INFLUENCE OF EXTERNAL PRESSURE	101
VIII.	BEHAVIOR DURING CHARGING AND DISCHARGING	106
IX.	REVERSIBILITY	119
X.	CHANGES IN THE OPEN CELL	129
XI.	INTERNAL RESISTANCE	147
XII.	CAPACITY	153
XIII.	DEGREE OF EFFICIENCY AND WORKING EFFICIENCY	174
XIV.	CHANGES IN THE CELL DURING FORMATION	185
XV.	METHODS OF MEASUREMENT	196
XVI.	TABLE OF DENSITY AND PERCENTAGE STRENGTH OF MIXTURES OF SULPHURIC ACID AND WATER	219

THEORY OF THE LEAD ACCUMULATOR.

I.

CHEMICAL THEORY OF ORIGIN OF CURRENT.

THE first attempt at a theoretical explanation of the changes in a lead accumulator we owe to the renowned inventor Gaston Planté, who laid down his views in a well-known work, "Recherches sur l'Electricité."[1] According to Planté, the chemical process in the lead secondary element consists essentially of an oxidation and reduction of the lead plates. During the charging the current decomposes the water into its constituents. The liberated oxygen then oxidizes the positive lead electrode to lead peroxide, while at the negative electrode the lead peroxide is reduced to lead sponge. During the discharging the lead peroxide again passes into a lower state of oxidation and the lead sponge is converted into oxide.

[1] German translation by Prof. Wallentin. Pub. Alfred Hoelder, Vienna, 1886.

This view was opposed by the English investigators J. H. Gladstone and A. Tribe on the ground of a careful chemical study of the active substances concerned in secondary elements. The results of their studies are contained in a very interesting monograph, "Die chemische Theorie der sekundaeren Batterien nach Planté und Faure."[1]

During their researches these investigators observed that the density of the accumulator acid diminishes during the discharging, increasing again during the charging; that the amount of the acid disappearing and forming respectively is approximately proportional to the amount of current passed through the element. Planté had likewise observed the change in the density of the acid, but did not follow it up.

Gladstone and Tribe concluded from this fact that during discharge the acid must have combined with the plates. They confirmed this surmise by analyses which showed that during discharge a quantity of lead sulphate, proportional to the amount of current, is formed. This fact could not be made to conform with Planté's views as to the current origin. Gladstone and Tribe therefore set up a new theory of the chemical processes in the secondary element, which later was called the "Sulphate Theory," and to the present day has victoriously withstood all attacks. According to this theory the electrolytic process

[1] German by Dr. R. v. Reichenbach. Pub. Hartleben, Vienna, 1884.

during discharge consists, as mentioned, in a formation of lead sulphate at both poles, and during charge in the oxidation and reduction of the sulphate to peroxide and lead sponge respectively.

The steps of the action at both electrodes can be represented as follows: During charging the dilute sulphuric acid is decomposed by the current into the radicals H_2 and SO_4; the former constituent is set free at the negative pole, the latter at the positive. The radicals then react with the lead sulphate according to the equations

$$PbSO_4 + H_2 = Pb + H_2SO_4 \text{ (neg. pole)},$$
$$PbSO_4 + SO_4 + 2H_2O = PbO_2 + 2H_2SO_4 \text{ (pos. pole)}.$$

During discharge the current flows through the cell in the opposite direction, so that now H_2 is set free at the peroxide electrode and SO_4 at the lead-sponge electrode; the reactions taking place being

$$Pb + SO_4 = PbSO_4 \text{ (neg. electrode)},$$
$$PbO_2 + H_2 + H_2SO_4 = PbSO_4 + 2H_2O \text{ (pos. electrode)}$$

so that after the discharge the surface of both plates is again converted into sulphate and the possibility of producing a current ceases. Combining the above four equations, we obtain the simple equation for the current producing chemical action in the lead accumulator:

$$PbO_2 + Pb + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O. \quad (1)$$

Reading the same from left to right gives us the change during discharge, and from right to left during charge.

Through this equation, as will be shown in that which follows, all the processes of both a physical and a chemical nature in the working accumulator during charge and discharge receive their best explanation, and for the most part can be quantitatively calculated in advance. In the following theoretical considerations, then, it will be necessary for us repeatedly to return to this fundamental equation as a starting-point. Since, even quite recently, doubts as to the correctness of the same have been harbored and new theories of the chemism set up, it is of primary importance, in order firmly to plant the foundation upon which we expect to build, to demonstrate as nearly as possible, in the light of the investigations at hand, the exactness of the equation. To do this we must show that the substances of equation (1) are in reality formed and decomposed in the accumulator in accordance with Faraday's law; secondly, that the decomposition and formation of all these substances has a part in the production of current corresponding to their energy contents, and is not partly the result of secondary decomposition, as has been assumed in several newer theories. In the following this proof is carried through for each substance separately.

(*a*) *Formation and Decomposition of Lead Peroxide and Lead.*

The fact that, during the electrolysis of dilute sulphuric acid between lead electrodes, lead peroxide and lead sponge are formed was first demonstrated in 1850 by Sinstedten. Since the lead sponge is directly visible, its formation has of late never been questioned. In place of the formation of lead peroxide, however, different investigators have assumed the formation of a hydrated lead peroxide (H_2PbO_3). An analysis can hardly decide which of the two substances is to be found upon the charged positive plate, because the hydrate very easily splits off water, thereby passing into peroxide. A safe decision can only be reached by means of the physical properties of the two substances, and above all through their different energy content, which is most apparent in the different electromotive behavior. Streintz[1] determined for this purpose the electromotive force of the different lead oxides against a zinc electrode, obtaining the following values:

Pb/Pb_2O —Zn = 0.42 volt
Pb/PbO —Zn = 0.46 "
Pb/Pb_3O_4 —Zn = 0.75 "
Pb/H_2PbO_3—Zn = 0.96 "
Pb/PbO_2 —Zn = 2.41 "

A charged positive accumulator plate has against zinc a potential difference of 2.4 volts, from which

[1] Wied. Ann. 38, p. 344. 1889.

it follows without a doubt that during charging we have formed on the positive electrode lead peroxide and not its hydrate. Later Strecker[1] studied the same question and showed that a plate covered with pure, chemically prepared peroxide gives, in dilute sulphuric acid, the same potential difference as a positive accumulator electrode. Such a plate could be discharged just as well as one in which the peroxide had been electrolytically produced.

In addition Strecker showed that the electromotive force of a positive electrode heated to 170° C., the temperature at which the hydrate is completely decomposed, remains unchanged. Streintz[2] believes to have observed the formation of black superoxyhydrate in several Planté cells, however only in very minute quantities and as a by-product. Detailed analytical investigations of the active mass have been made by Ayrton, Lamb, and Smith.[3]

From a positive accumulator electrode during charging and discharging several samples of the active mass were taken and the amount of PbO_2 contained in them determined. In this way the percentages of PbO_2 shown in Fig. 1 were obtained.

The quantities of peroxide contained in the active mass increase and decrease very nearly

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[1] Elektrotechn. Zeitschr. 1891, pp. 435, 513, 524.
[2] Wied. Ann. 46, p. 449. 1892.
[3] Elektrotechn. Zeitschr. 1891, p. 66.

proportionally with the amount of current passed through the cell.

(*b*) *Formation and Decomposition of Lead Sulphate and Sulphuric Acid.*

The quantitative demonstration of the formation of lead sulphate was furnished by Gladstone and

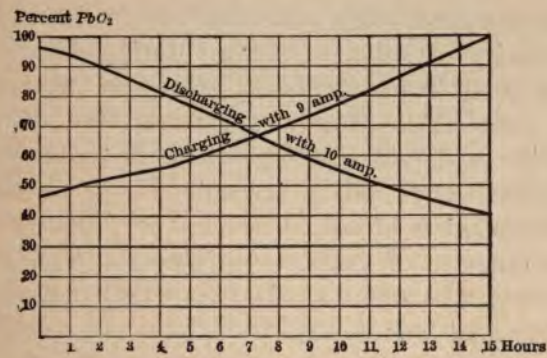

FIG. 1.

Tribe through the analyses of the active mass. At the same time, the recently often questioned fact was established that sulphate is formed at both electrodes, proportional to the amount of electricity taken out. Ayrton, Lamb, and Smith arrived at this same result in their analytical investigations mentioned above. Frankland expressed himself against the formation of $PbSO_4$ and surmised the presence of other sulphuric acid compounds of the composition, for example, of $Pb_5S_3O_{14}$ and the like. Shortly afterward Gladstone and Hib-

bert[1] by their searching investigation proved that the sulphates of Frankland are not compounds, but mixtures of lead sulphate and lead peroxide.

Ayrton arrived at the same results through the investigations he had Robertson[2] carry out on the active mass of plates discharged to 1.6 volts. This analysis gave 47.3 per cent PbO_2 and 50.74 per cent $PbSO_4$.

A simpler and more accurate way to determine the quantity of sulphate formed during discharge than is possible by the analysis of the substance of the electrode is from the consumption of the sulphuric acid surrounding the electrodes. As already mentioned, Gladstone and Tribe found that the consumption of sulphuric acid is proportional to the amount of current withdrawn. The first attempt to measure quantitatively this consumed sulphuric acid was made by Aron;[3] the most accurate determination, however, we owe to W. Kohlrausch and C. Heim.[4] Since these measurements are of great importance to the theory of the accumulator, and since even to-day the quantitative sulphate formation is doubted, though incomprehensibly, they are given here in detail.

An accumulator of the firm of Buesche and Mueller in Hagen i. W.[5] was charged with 5 amp. and dis-

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[1] Chem. News, 65. 1892.
[2] Proc. Roy. Soc. 50, p. 105. 1891.
[3] Elektrotechn. Zeitschr. 1883, pp. 58 and 100.
[4] *Ibid.* 1889, p. 327.
[5] Now Accumulatoren-Fabrik-Aktiengesellschaft, Hagen i. W.

charged with 6.5 amp.; at the same time the density of the acid was measured by means of an hydrometer. The acid density fell and rose almost exactly in proportion to the amount of electricity flowing through the cell, as Fig. 2 shows.

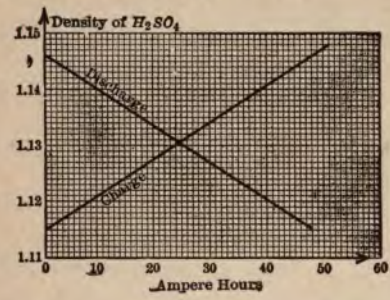

FIG. 2.

If we assume that the chemical action in the accumulator is according to our fundamental equation (1), then charging removes two molecules of water and forms two molecules of sulphuric acid; discharging effects the reverse. The change in density in the accumulator is calculated therefore as follows:

The uncharged storage battery contains 3350 c.c. of acid of sp. gr. 1.115, i.e., 16.32 per cent sulphuric acid.

The bath therefore weighs

$$3350 \times 1.115 = 3735 \text{ g.},$$

and contains

$$0.1632 \times 3735 = 610 \text{ g. } H_2SO_4$$

hence 3125 g. water.

As a result of a charging current of 50 ampere-hours there disappear, according to the above conception,

$$50 \times 2 \times 0.336 = 33.6 \text{ g. water,}$$

and there are formed

$$33.6 \times \frac{98}{18} = 183 \text{ g. } H_2SO_4.$$

The bath therefore contains, after charging with 50 ampere-hours,

$$3125 - 33.6 = 3091.4 \text{ g. water}$$

and

$$610 + 183 = \underline{\quad 793 \quad} \text{ g. } H_2SO_4$$

weighing 3884.4 g.

The percentage strength is therefore

$$\frac{793}{3884.4} = 20.42 \text{ per cent}$$

and the density 1.146. From this the volume of the liquid after charging is calculated to be

$$\frac{3884}{1.146} = 3389 \text{ c.c.}$$

Actual observation has given the density after charging with 50 ampere-hours as 1.147.

In the case of this particular accumulator we have then for a charge of 1 ampere-hour practically exactly 3.66 g.—the theoretical requirement of sulphuric acid formed.

Recently Mugdan,[1] in a very interesting research upon the accumulator, has described several experiments concerning the formation of sulphate. Small and well-formed, charged Pollak plates were discharged in various strengths of sulphuric acid, with a current density of 0.02 amp./sq. cm., and the quantity of sulphate formed determined. Table I gives the quantities found.

TABLE I.

	Sulphate Formation in Per Cent of the Theoretical.	
	Pos. Plate.	Neg. Plate.
1. Pollak-plate discharged in 26% acid.....	94.0	100.0
2. Pollak-plate discharged in 10% acid.....	90.1	98.7
3. Pollak-plate not discharged in 26% acid.	—	—
4. Perforated grid plates not discharged in 26% acid.....	—	—
5. Perforated grid plates discharged in 10% acid.....	(80.3)	(21.7)
6. Perforated grid plates discharged in 14% Na_2SO_4 solution.....	—	(70.4)

The potential of the plates 5 and 6 decreased long before the end of the discharge on account of their smaller capacity; consequently as far as the quantitative side of the measurements is concerned only plates 1 and 2 need to be considered. The values obtained for these plates prove that even in 10 per cent acid with the high current density of 0.02 amp./sq. cm. and a complete discharge in the technical sense in only twenty minutes, lead sulphate is essentially formed, as the theory demands, on the negative and positive plates.

[1] Zeitschr. f. Elektrochem. 1889, H. 23.

Discharging in sodium sulphate solution, it is clear, leads to the formation on the positive plate of oxide only. On the negative plate, however, the formation of sulphate is recognizable.

According to the already mentioned measurements of W. Kohlrausch, Heim, and Mugdan we cannot doubt the formation of sulphate at both electrodes. It yet remains, however, to prove that this sulphate formation (at both electrodes) also contributes its share to the production of current, corresponding to its energy of formation, and is not, partly or wholly, the result of non-current producing reactions. This proof has likewise, repeatedly and very exactly, been made. It should be stated here that the thermochemical investigations of Tscheltzow and Streintz, which are to be considered in detail in the following chapter, have given the result that the electromotive force calculated from the heat of reaction only agrees with the actual when we assume the formation of sulphate at both electrodes. Recently I have further shown that the change of electromotive force with the acid concentration exactly coincides with the change in the free energy which 2 molecules undergo when we bring them from one concentration to another.[1] The degree of the change of the electromotive force with the acid density is therefore also a very exact proof that the sulphate formation is current-producing, i.e., takes place primarily and not secondarily.

[1] Compare Chapter IV.

(c) *Formation of Water.*

It still remains to be determined whether the formation of water takes place according to our reaction equation and is active electromotively. The fact of the formation of water follows directly from the above measurements and calculations of Kohlrausch and Heim. In addition the same, as also its share in the production of current, can be shown by the measurements of the electromotive force of the individual accumulator electrodes against a hydrogen electrode at different acid concentrations which I recently carried out.[1] We get in that way the two galvanic combinations PbO_2—H_2 and Pb—H_2, in which during discharging the two following reactions take place:

$$PbO_2 + H_2 + H_2SO_4 = PbSO_4 + 2H_2O,$$
$$Pb + H_2SO_4 = PbSO_4 + H_2.$$

During current production, then, there is consumed in both cells one molecule of H_2SO_4, the PbO_2—H_2 element forming in addition two molecules of water. Therefore, as a simple consideration in energetics shows, the electromotive forces of these two combinations, in their dependence upon the acid concentration, must vary only in the measure of the change of the energy of formation of water in different concentrations of sulphuric acid. Since the electromotive forces calculated on the basis of

[1] Compare Chapter V.

the above agree excellently with those measured, there can be no doubt that the formation of water from the peroxide has its share in the production of current in the lead accumulator.

The experimental results contained in the above give the conclusive proof that the chemical reaction taking place in the accumulator can only be the one expressed by the equation

$$PbO_2 + Pb + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O,$$

and that primarily the consumption and formation of these substances takes place (during current production). If, however, the accumulator is subjected to very high current densities, then side reactions can set in, which under normal conditions are impossible. For example, by very rapid discharging the exhaustion of the acid in the active mass is so great that a formation of sulphate can no longer take place. The active mass in this case is only oxidized and reduced to lead hydroxide according to the equation

$$PbO_2 + Pb + 2H_2O = 2Pb(OH)_2.$$

Of course, then, the accumulator works irreversibly with a very poor efficiency coefficient, and the electromotive force is only about 1 volt. Charging, on the other hand, with great current density, the acid, as we shall see later, can be greatly concentrated at the electrodes, especially at the positive, so that a formation of persulphuric acid at the posi-

tive and a reduction at the negative of sulphuric acid to sulphur dioxide to hydrogen sulphide, indeed even down to sulphur, becomes possible. The formation of these decomposition products of sulphuric acid can be easily demonstrated by filling an accumulator with very concentrated acid (70 per cent H_2SO_4) and charging with high current density. Then the acid in proximity to the positive electrode turns potassium iodide starch blue, while at the negative electrode hydrogen sulphide and white sulphur are copiously liberated. The formation of these substances, however, takes place only under such abnormal conditions; normally they are not detectable.

There remains to be considered one more point which, so to speak, forms the life-question of the lead accumulator and has been recently discussed in detail by Nernst.[1] The electrolysis of dilute sulphuric acid between platinum electrodes gives at a voltage of 1.7 a weak, and at a voltage of 1.9 a strong, evolution of gas at both electrodes. One would suppose it impossible, then, to construct an accumulator, with dilute sulphuric acid as electrolyte, whose electromotive force lies above 1.7 volts, since at this voltage the electrolyte decomposes into its constituents. If, however, you substitute lead electrodes for those of platinum, a continuous current is first obtained at a pressure of 2 volts and the products of the electrolysis are not hydro-

[1] Zeitschr. f. Elektrochem. 1900.

gen and oxygen, but lead and lead peroxide. Not until the traces of lead sulphate present have been used up do we have, at a voltage of 2.3, an evolution of gas setting in. The formation of lead and lead peroxide out of lead sulphate takes place in this case at a considerably lower voltage than the decomposition of water. That is, electrolysis gives, of the possible products, not those obtainable by the least work, but those of considerably greater energy contents, viz., $Pb + PbO_2$, instead of the explosive mixture of hydrogen and oxygen ("Knallgas"). The explanation of this abnormal behavior of lead, which makes it possible to construct an accumulator of 2 volts, follows readily enough from the recent theory of Nernst for the evolution of hydrogen on metals, as tested by the experiments of Caspari.[1]

According to this theory there is to be added to the minimum pressure (free energy of formation) necessary to decompose an electrolyte an additive factor which takes into account a specific property of the electrode substance and which, as shown by the experiments, is greater as the power of the metal of the electrode for absorbing hydrogen is less. It appears, therefore, that the work necessary to produce bubbles of hydrogen on a metal surface diminishes very greatly with the occlusion power.

We have a large number of investigations upon

[1] Zeitschr. physikal. Chem. XXX, H. 1, p. 89 (1899).

the occlusion of hydrogen by lead,[1] all of which have shown that lead as compared with other metals has the power of occluding very little or no hydrogen. The work necessary to produce bubbles of hydrogen will therefore be very considerably greater on a lead than on a platinum surface, and that is why in the electrolysis of dilute sulphuric acid containing lead sulphate we have lead formed and not hydrogen.

That such are the facts is proven by the following simple experiment: A platinum dish and a lead dish, of equal size, were arranged as cathodes, in series, in a circuit. Both dishes contained solid lead sulphate covered with dilute sulphuric acid; a platinum wire spiral served in both cases as anode. A current of 0.02 amp. (current density about 0.0004 amp./sq. cm.) was passed through the dishes.

At this current density the lead dish had a potential difference of 1.92 volts against a lead peroxide electrode dipped into the acid, while the platinum dish showed only 1.60 volts. These voltage measurements in themselves indicated that a reduction of lead sulphate in the platinum dish was out of the question. This conclusion is confirmed by the fact that, after passing the current

[1] G. Meyer, Wied. Ann. 33, p. 278. 1888.—Frankland, Proc. Roy. Soc. XXXV, p. 67.—Gladstone and Tribe, On the Chemistry of Secondary Batteries, p. 48.—Streintz u. Anlinger, Wied. Ann. 38, p. 355.—Cantor, Monatshefte für Chemie, 11, p. 444.—Shields, Chem. News 65, p. 193. 1892.—Scott, Wied. Ann. 67, p. 388. 1899.

for three weeks, the lead sulphate in the platinum dish remained entirely unchanged, while that in the lead dish was almost completely reduced to lead sponge. If in the above experiment we increase the current density to 0.001 amp./sq. cm., the hydrogen is also formed on the platinum surface at such a high pressure that a reduction of lead sulphate takes place. It is most likely that a similar consideration holds good for the separation of oxygen; at any rate a strong retardation (Verzögerung) is beyond a doubt.

DARRIEUS' THEORY OF THE ORIGIN OF THE CURRENT.

Darrieus[1] in 1892, in a number of papers, expressed himself against this sulphate theory as developed in the previous paragraphs, and evolved a new theory of the chemical changes in the lead accumulator. Beginning with the fact, found by Berthelot, that when conc. H_2SO_4 is electrolyzed with a current of high density persulphuric acid is formed, Darrieus assumes that, charging the accumulator in dilute acid, persulphuric acid is primarily formed, which then secondarily reacts with the lead sulphate to form peroxide and sulphuric acid, according to the equation

$$H_2S_2O_8 + PbSO_4 + 2H_2O = PbO_2 + 3H_2SO_4.$$

[1] Lum. Electr. 44, p. 513. 1892. Compare also Schoop, Zeitschr. f. Elektrochem. 1894, p. 293. Schoop, Handbuch der Accumulatoren 1898, p. 487.

The change at the negative electrode he considers, like Gladstone and Tribe, as a reduction of the lead sulphate to metallic lead. Concerning the action during discharge Darrieus, however, is likewise of a different opinion. He believes that at the lead-sponge electrode lead suboxide and at the peroxide electrode lead oxide are primarily formed, which substances secondarily react with the sulphuric acid to form sulphates, as expressed by the equations

$$Pb_2O + H_2SO_4 = Pb + PbSO_4 + H_2O,$$
$$PbO + H_2SO_4 = PbSO_4 + H_2O.$$

Darrieus has undertaken to confirm his hypothesis by experiments. However, since most of these contradict themselves and later have been directly disproven by prominent investigators, it will be unnecessary to give them here. Gladstone and Hibbert [1] were the first to turn against the theory of Darrieus in that they showed that an addition of persulphuric to the anode acid does not, as Darrieus maintained, and as directly follows from his theory, cause an increase, but rather a decrease, of the electromotive force. We are indebted to Elbs and Schoenherr [2] for careful and interesting investigations upon the formation of persulphuric acid. They have shown that per-

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[1] Chem. News 65, p. 309. 1892.

[2] Zeitschr. f. Elektrochem. 1895, pp. 417, 473, and 1896, pp. 245, 471.

sulphuric acid forms in large quantities only in comparatively concentrated sulphuric acid (density 1.3 to 1.5), while in dilute acids, such as are employed in accumulators, only very small amounts can form. In addition it was found that the current density greatly influences the amount. Employing an acid of the concentration used in accumulators (density 1.15), Elbs and Schoenherr obtained, with a current density equal to 1 amp./sq. cm., 7 per cent of the theoretical amount of persulphuric acid; with 0.5 amp. current density the persulphuric acid could not be determined. Since the accumulator can be charged with as small a current density as you please, it follows that under normal conditions no persulphuric acid is formed.

Recently Mugdan [1] has experimentally disproven the experiments of Darrieus. He found, just as did Gladstone and Hibbert, that an addition of persulphuric acid does not raise but lowers the electromotive force of the accumulator. Persulphuric acid is unable to oxidize lead sulphate to peroxide, but, quite the reverse, deoxidizes peroxide to sulphate, with the evolution of oxygen containing ozone. More than that, Mugdan has shown by direct experiment that even with an acid of only 4.9 per cent strength and the abnormally high discharging densities of 0.018 to 0.025 amp./sq. cm. no detectable quantities of oxide or suboxide, as Darrieus assumes, but only sulphate, is formed.

[1] Zeitschr. f. Elektrochem. 1899, p. 309.

In spite of the fact that the investigations referred to show the invalidity of the theory of Darrieus, it may be well to mention that a consideration from the standpoint of energetics also gives a direct proof of the untenability of the same. The spontaneous formation of the peroxide from persulphuric acid and lead sulphate, as well as the formation of the $PbSO_4$ from Pb_2O or PbO and H_2SO_4, is necessarily associated with a large loss of energy. Such a loss, however, stands in direct contradiction to the fact that the accumulator is absolutely reversible (without loss of energy) with small current densities (see Chapter IX). In addition to this, according to the theory of Darrieus, sulphuric acid is not (primarily) set free during charging, but, on the contrary, is consumed in the formation of persulphuric acid. The charging voltage would, therefore, have to be lower with increasing concentration of acid, which is likewise contrary to the facts.

ELBS' THEORY OF THE ORIGIN OF THE CURRENT.

Elbs [1] has developed a very ingenious conception, diverging from the pure sulphate theory, of the chemical changes taking place at the anode of a lead accumulator. The possibility of the lectrolytic preparation of lead tetracetate ($Pb(CH_3COO)_4$) from lead diacetate ($Pb(CH_3COO)_2$), led to the assumption that in the accumulator the sulphate

[1] Zeitschr. f. Elektrochem. 3, p. 70. 1896.

of tetravalent lead, lead disulphate, $Pb(SO_4)_2$, is primarily formed, which then secondarily reacts with water, being converted into peroxide and sulphuric acid. During charging the immediate reaction at the anode is

$$PbSO_4 + SO_4 = Pb(SO_4)_2,$$

followed by

$$Pb(SO_4)_2 + 2H_2O = PbO_2 + 2H_2SO_4.$$

For discharging he likewise assumes the formation of lead sulphate from peroxide and lead.

The above spontaneous decomposition of lead disulphate is, however, as Nernst [1] has pointed out, a non-reversible change, which can only take place at a not inconsiderable loss of free energy. The Elbs theory likewise represents the accumulator as an irreversible element and is therefore untenable, as will be shown later. Also the fact that the charging voltage rises greatly with the acid concentration stands in contradiction to the theory of Elbs.

In accordance with this theory the charging action, considered at both electrodes at the same time, can be represented by the simple equation

$$2PbSO_4 = Pb(SO_4)_2 + Pb.$$

By this equation, on the whole, neither sulphuric acid is given up to nor taken from the electrolyte

[1] Zeitschr. f. Elektrochem. 3, p. 78.

during charging. Now since $PbSO_4$ is present in the solid form, and therefore the fre energy of the dissolved sulphate constant (equal to that of the solid salt), the affinity of the above reaction, and therefore also the charging voltage, would have to be independent of the acid concentration, which is not the case, as has already been mentioned.

Recently lead disulphate and a double salt of the same have been prepared in the laboratory of Prof. Elbs. The salt, like the isomer lead persulphate, immediately decomposes into lead peroxide and sulphuric acid upon treatment with water, as was demonstrated by Elbs at the Sixth Meeting of the German Electrochemical Society. The preparation, however, of the lead disulphate [1] did not take place under conditions as they prevail in the accumulator, so that this highly interesting chemical investigation does not, as Nernst [2] has pointed out, permit of a conclusion as to the action in a lead accumulator.

The loss of energy which is associated with the decomposition of the lead disulphate could be easily determined by measuring the quantity of heat liberated, when 1 g.-mol. of lead disulphate is treated with accumulator acid. Since the temperature coefficient of the accumulator is very small, this simple calorimetric measurement would allow the energy loss, which would have to occur

[1] Unfortunately at present more definite directions are not available.

[2] Zeitschr. f. Elektrochem. VI, p. 46. 1899.

if the chemical action took place in the way given, to be expressed in volts. Such a measurement would very probably give several hundredths or possibly tenths volts, which conclusion follows from the speed with which the decomposition takes place. Such a loss of energy is, however, irreconcilable with the absolute reversibility of the accumulator when working with small current densities.

II.

THERMODYNAMICAL THEORY OF ORIGIN OF CURRENT.

As we have seen in the previous chapter, the electrical energy is not stored in the accumulator as such, but in the form of potential chemical energy, which during the production of current has first to be transformed into electrical energy. It is necessary, then, to next concern ourselves with the laws which determine the transformation of chemical into electrical energy and vice versa. The total change of energy which accompanies a chemical action is given, as is well known, by the heat of reaction. If, instead of in a calorimeter, we allow the reaction to take place in a galvanic cell (and the charged accumulator is one), we obtain a certain amount of electrical energy, which we can quantitatively transform into work. This work represents, according to Helmholtz, the "free energy." According to the second law of thermodynamics there exists the following relation between Q, the heat effect of a reaction, and W, the change in free energy (maximum work):

$$W = Q + T\frac{\partial W}{\partial T}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which T stands for absolute temperature, and therefore $\frac{\partial W}{\partial T}$ for the temperature coefficient of the working capacity of the system. If the heat effect is referred, as is usual, to 1 g.-equivalent of the reacting substance, then we must introduce for W the electrical energy which corresponds to 1 g.-equivalent of the substance changed, i.e., if E is the electromotive force of the accumulator.

$$W = 96540.E \text{ volt-coulombs.}^1$$

Noting that 1 volt-coulomb is equivalent to 0.239 g.-cal., the second law gives, as the relation between heat effect and electromotive force, the expression

$$E = \frac{Q}{23073} + T\frac{\partial E}{\partial T} \text{ volts.} \quad . \quad . \quad . \quad (3)$$

This equation, developed by v. Helmholtz in the year 1882, permits the calculation of the electromotive force from the heat effect of the current-producing reaction, and the temperature coefficient of the electromotive force, or the temperature coefficient from E and Q. It has, since its discovery, found numerous applications and confirmations.

Let us apply the same to the accumulator, first, in the simplest possible case. As we shall see in

[1] Since, according to the law of Faraday, 96540 coulombs bring about the reaction of 1 g.-equivalent of a chemical substance.

the chapter on "Temperature Coefficient," the electromotive force of the accumulator becomes independent of the temperature at an acid density of 1.044 (15° C.) (0.70 g.-mol. H_2SO_4 per liter), i.e., in this case $\frac{\partial E}{\partial T}=0$. We have then as holding for the named density (and only for the particular density) the simple relation (Thomson's rule)

$$E=\frac{Q}{23073}\text{ volts}, \quad . \quad . \quad . \quad . \quad (4)$$

in which is to be inserted for Q the heat effect for 1 g.-equivalent of our reaction equation:

$$PbO_2+Pb+2H_2SO_4=2PbSO_4+2H_2O.$$

The determination of the heat value Q of this reaction we owe again to that well-deserving investigator in the field of the accumulator theory, Fr. Streintz,[1] and the French physicist Tscheltzow.[2] The investigators just named were also the first to calculate, by means of the above equation, the electromotive force of the accumulator. Since the reaction of the solid substances, lead peroxide and lead, takes place very slowly, a direct calorimetric determination of the heat of reaction cannot be made. The reaction must be brought about indirectly. Streintz for this purpose determined the heat of reduction of lead peroxide by a mixture

[1] Wied. Ann. 53, p. 698. 1894.
[2] Compt. rend. 100, p. 1458. 1885.

of aqueous sulphurous and hydrochloric acids, in which peroxide converts into sulphate. The heat effect of this reaction was found to be

$$PbO_2 + H_2SO_3\,aq = PbSO_4 + Aq + 76700 \text{ cal.} \quad (5)$$

According to Thomsen,[1] the heat of oxidation of sulphurous acid is

$$H_2SO_3\,aq + O = H_2SO_4\,aq + 63600 \text{ cal.} \quad (6)$$

Subtracting equation (6) from (5), we get

$$PbO_2 - O + H_2SO_4\,aq = PbSO_4 + Aq + 13100 \text{ cal.} \quad (7)$$

For the oxidation of lead to lead oxide and the neutralization of the oxide to sulphate, Thomsen found the heat value

$$Pb + O + H_2SO_4\,a = PbSO_4 + Aq + 73700 \text{ cal.}, \quad (8)$$

from which, by addition with (7), we get finally the heat effect for the accumulator reaction:

$$PbO_2 + Pb + 2H_2SO_4\,aq = 2PbSO_4 + Aq + 86800 \text{ cal.} \quad (9)$$

Tscheltzow also measured the heat of reduction of lead peroxide by sulphurous acid (gaseous form) and found

$$PbO_2 + SO_2\,gas = PbSO_4 + 82600 \text{ cal.}$$

[1] Thermochemische Untersuchungen.

In addition he determined the heat of oxidation of mercurous nitrate by lead peroxide and obtained

$$PbO_2 + 2HgNO_3 + 4HNO_3 = Pb(NO_3)_2 + 2Hg(NO_3)_2 + 2H_2O + 31800 \text{ cal.}$$

The heat of formation of lead peroxide calculated from these figures is

$$PbO + O = PbO_2 \quad 12100 \text{ cal.},$$

while the value from the measurements of Streintz is

$$PbO + O = PbO_2 + 10100 \text{ cal.}$$

Therefore the heat effect of the accumulator reaction is, according to the measurements of Tscheltzow, somewhat higher than Streintz's value, being 88800 cal. In addition, we must remember that the above employed thermochemical data of Thomsen are for very dilute sulphuric acid (1 mol. H_2SO_4 to about 400 mol. H_2O). If we wish to calculate the electromotive force for a certain acid concentration, we must also take into consideration the heat of dilution of the sulphuric acid. For the acid density 1.044 at which the simple expression (4) holds good we must subtract a heat of dilution

$$2(H_2SO_4, 78H_2O) = 2(H_2SO_4, 400H_2O) + 1056 \text{ cal.}$$

Consequently we have

$$2Q = 85700 \text{ cal. and } 8\ 700 \text{ cal.},$$

and the electromotive force of the accumulator according to equation (4):

$$E = 1.86 \text{ volts (Streintz)},$$
$$E = 1.90 \text{ volts (Tscheltzow)}.$$

The measurement for this acid density gives the value 1.89 to 1.90 volts, in excellent agreement with the above. (Compare Chapter IV.)

A calculation of the electromotive force of the accumulator for the density 1.15 ($1H_2SO_4 + 21H_2O$), the acid density commonly used, cannot be carried out with equation (4), but only by means of equation (3), because in this case the member $T\frac{\partial E}{\partial T}$ possesses a considerable value. At this concentration we have to subtract the very considerably larger heat of dilution, 1600 cal., and we get

$$2Q = 85200 \text{ cal. and } 87200 \text{ cal.}, \quad T = 290,$$

$$\frac{\partial E}{\partial T} = +0.4 \times 10^{-3} \text{ (compare Chapter VI)},$$

from which the calculated electromotive force is

$$E = 1.96 \text{ and } 2.01 \text{ volts respectively},$$

while the real (observed) electromotive force is 1.99 to 2.01.

As a third example let us carry out a calculation

for a very dilute acid, 0.01 g.-mol. H_2SO_4 per liter, for which the electromotive force is only 1.66 volts (18° C.). At this acid concentration we have to add to the above thermochemical data a heat of dilution equal to 1088 cal. We have then

$2Q = 87900$ cal. and 89900 cal., $\frac{\partial E}{\partial T} =$ about -0.001 (see Chapter VI), from which by means of equation (3) we get a value equal to 1.63 volts, which is a close enough agreement with the observed electromotive force when we consider the uncertainty of the value of $\frac{\partial E}{\partial T}$. In this instance the member $T\frac{\partial E}{\partial T}$ is equal to -0.29 volt, so that a calculation according to equation (4), from the heat effect alone, would therefore lead to an entirely incorrect result. Even though the heat effect increases with the dilution of the acid, the electromotive force nevertheless rapidly decreases.

The fact that the electromotive forces calculated on a purely energetic basis from the heat of reaction agree so well with those actually observed is, as was pointed out in the previous chapter, conclusive evidence that the chemical actions in the accumulator can only be those represented by our fundamental equation (1) and no others. One often finds the opinion expressed that the primary formation of sulphate takes place (during current production) only on the lead-sponge electrode, while on the peroxide electrode it is formed second-

arily by the action of sulphuric acid upon the primarily formed oxide. Equation (3) allows the testing of this opinion as to its correctness. If the process of discharging takes place in the way just indicated, the corresponding heat of reaction is smaller by

$$PbO + H_2SO_4\,aq = PbSO_4 + Aq + 23400 \text{ cal.}$$

than the value given above. The electromotive force calculated is then 1.32 volts instead of 1.9 volts. The possibility of a one-sided primary sulphate formation is therefore excluded.

The member $T\frac{\partial E}{\partial T}$ in equation (3) is called the secondary or latent heat of a galvanic element, because it represents the heat which the working element takes from or gives up to its surroundings, according to its algebraic sign. At the acid concentration usually employed in the lead accumulator the electrical energy is greater than the heat effect and consequently $\frac{\partial E}{\partial T}$ is positive; from which it follows that the accumulator must work during discharging with an absorption of heat and during charging with a liberation of heat, as direct temperature measurements by Duncan have demonstrated. As will be shown in the chapter on temperature coefficient, just the reverse takes place when the acid is diluted.

Exact quantitative measurements of the secondary heat of accumulators have been carried out by Streintz.[1] A small cell with electrodes 9.3×1.6 cm. in size cut from Tudor plates was placed in the reaction-tube of a Bunsen ice-calorimeter, charged and discharged with a weak current of constant strength and the developed quantity of heat determined. The heat developed during discharging is made up of the difference between the Joule heat set free in the element and the secondary heat, and during charging of the sum of the same. If the latter heat be indicated by S, the current strength by i, and the inner resistance of the cell, to be taken as small as possible, by r, we have as the heat developed in the accumulator during discharging

$$q = i^2 r - Si \text{ watt-sec.},$$

and during charging

$$q' = i^2 r + Si \text{ watt-sec.}$$

The influence of the Joule heat we can easily avoid, as Streintz did, by taking r and i very small and measuring the heat developed both during charging and discharging. If the current strength i is taken equal in both cases, we get for S the equation

$$S = \frac{1}{2i}(q' - q) = T\frac{\partial E}{\partial T}.$$

[1] Wied. Ann. 49, p. 564. 1893.

The results of Streintz's investigations are given in Table II.

TABLE II.

Acid Density.	E Volts.	Current-strength, i Amp.	Heat-evolution, Watt-sec.		Duration, Minutes.	Second. Heat, S, Watt-sec.	
			Discharge, q.	Charge, q'.		Found.	Calculated.
1.155	1.99	0.100	0.0040	0.0228	61	0.094	0.089
1.153	1.99	0.0678	0.00159	0.0137	120	0.089	0.086
1.237	2.07	0.0729	0.00547	0.01225	60	0.046	0.041

The last column contains the secondary heat values calculated from the temperature coefficients (compare Chapter VI). The agreement of these with the calorimetric measurements is very satisfactory when we consider the small quantities of heat we have to deal with. These measurements, however, are only for concentrated acids. It would no doubt be very interesting to carry out a determination of the secondary heat with very dilute acid, for then the same, as will be shown later, assumes very large but negative values. Such measurements could only be made to give accurate results with extremely small current densities, for otherwise large concentration changes of the acid at the electrodes would occur, which in their adjustment would develop considerable quantities of heat. The error introduced thereby in such calorimetric measurements is often very

much greater than the one caused by the internal resistance.

We shall learn of further applications of thermodynamics to the lead accumulator in Chapters IV, V, VI, and VII.

III.

OSMOTIC THEORY OF ORIGIN OF CURRENT.

THE previous thermodynamical discussions enabled one to determine definitely the current-producing chemical process, but they do not give one a deeper insight into the origin of the potential difference. The latter can only be hoped for through the application of Nernst's newer "Osmotic Theory" of the galvanic element. The Nernst theory therefore is of the greatest importance to lead accumulators, and it will be necessary to become familiar with the fundamental concepts of the same.

If any piece of metal be int oduced into an electrolyte, a potential difference between metal and liquid is established, which tends to produce a current of such direction that metal passes into the electrolyte. The fact that this potential difference appears of its own accord shows that every metal, similar to a soluble salt, possesses a strong tendency to pass into solution, i.e., into the ionic state. Nernst has very appropriately designated this property of metals electrolytic solution tension.

As soon as salt of the metal has formed in the liquid surrounding it, the potential difference diminishes, since the osmotic pressure of the metal ions acts against the solution tension. If we increase still further the concentration of the metal ions, the potential difference will finally become zero, as soon as the counter-osmotic pressure of the metal ions has become equal to the solution tension. The solution tension of such an ionic solution is therefore energetically equal to its osmotic pressure. The magnitude of the potential difference which appears at the point of contact between a metal and the solution of one of its salts is given according to Nernst's theory as follows: If we allow $1F = 96540$ coulombs of electricity to pass from the metal into the solution, which, according to Faraday's law, is equal to dissolving 1 g.-equivalent of the metal, an amount of work $\varepsilon . F$ volt-coulombs is performed, if ε designates the potential difference sought. At the same time $\frac{1}{n}$ g.-ions of the metal (n = valence) are brought from the solution pressure P to the osmotic pressure p of the ions in solution, which is equivalent to the work $\frac{RT}{n} ln \frac{P}{p}$.[1] Since the dissolving of a metal

[1] If 1 g.-mol. of a gas or a substance in solution is brought from the gas or osmotic pressure p to the pressure $p - dp$, the work $dW = vdp$ is performed, v denoting volume. Now according to the gas law, which is, according to van't Hoff, also applicable to the osmotic pressure in dilute solutions,

can be reversibly conducted, the electrical work must be equal to the osmotic. If we express the gas constant R in units of electrical energy and employ Briggs's logarithms, we get

$$\varepsilon = \frac{RT}{n} ln \frac{P}{p} = \frac{0.0001983}{n} T \log^{10} \frac{P}{p} \text{ volts.}$$

In dilute solutions the osmotic pressure is proportional to the ion concentration; we can therefore substitute for the pressure ratio the concentration ratio and get

$$\varepsilon = \frac{0.0001983}{n} T \log^{10} \frac{C}{c} \text{ volts,} \quad . \quad . \quad . \quad (10)$$

in which C indicates the ion concentration which is in equilibrium with the solution tension. In the future we will for convenience refer to the concentration C as solution tension. Equation (10), developed by Nernst in 1889, along with the above thermodynamical relations of H. v. Helmholtz, forms the foundation of modern electrochemistry, and has in the past found numerous applications and various confirmations. In that which is to

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$v = \frac{RT}{p}$ (R = gas constant, T = absolute temperature); we have then $dW = RT\frac{dp}{p}$. In the change from the pressure P to the smaller pressure p the amount of work performed is

$$W = RT \int_p^P \frac{dp}{p} = RT ln \frac{P}{p}.$$

follow we will become acquainted with the fruitfulness of these, in their application to the lead accumulator.

Le Blanc was the first to apply the ion theory to the accumulator. In his book on electrochemistry he gives the first explanation of the production of current in the lead accumulator on the basis of this theory. One year later Liebenow developed a somewhat different theory of the production of current. Since at present there exists no good ground for giving one or the other theory preference, and as we are compelled to consider both of equal value, both views involved will be presented here. The only advantage that the theory of Liebenow has over the older one of Le Blanc is its simplicity and the fact that it is more readily expressed in exact formulæ.

Theory of Le Blanc.

In order to explain the origin of the electromotive force in the accumulator, Le Blanc assumes that lead peroxide, like every other substance, has a definite solubility in water. This peroxide then reacts with the water to form tetravalent lead ions and hydroxyl ions, according to the equation

$$PbO_2 + 2H_2O = \overset{++}{\underset{++}{Pb}} + 4\overset{-}{OH}.$$

Then during discharging the tetravalent lead ions give up two charges to the electrode and combine

with one $\bar{\bar{S}}\bar{\bar{O}}_4$ ion of the sulphuric acid to produce solid sulphate. At the same time at the lead-sponge electrode the two charges which are taken from the electrolyte at the positive electrode are given back to it in the form of a $\overset{++}{Pb}$ ion, which latter combines with one $\bar{\bar{S}}\bar{\bar{O}}_4$ ion to give solid sulphate. The liberated $\overset{+}{H}$ ions of the acid form water with the $\bar{O}\bar{H}$ ions. According to the theory of Le Blanc we can therefore express the process of discharging by the reversible equations

$$PbO_2 + 2H_2O = \overset{++}{Pb} + 4\bar{O}\bar{H},$$

$$\overset{++}{Pb} + Pb + 2\bar{\bar{S}}\bar{\bar{O}}_4 = 2PbSO_4,$$

$$4\bar{O}\bar{H} + 4\overset{+}{H} = 4H_2O.$$

If all the peroxide and lead are consumed, we have lead sulphate at both electrodes.

During the charging of the cell we have conversely, at the positive pole, the bivalent lead ions, coming from the sulphate, converted into $\overset{++}{Pb}$ ions by taking up electricity. These ions, then, as soon as their concentration corresponds to that of the solubility of the peroxide, react with the water, forming lead peroxide. At the negative electrode

the $\overset{++}{Pb}$ ions pass into the metallic state by giving up their charges. The process of charging the cell can be represented by the equations

$$2PbSO_{4\,solid} = 2\overset{++}{Pb} + 2\overset{--}{SO_4},$$

$$2\overset{++}{Pb} = \overset{++}{Pb} + Pb,$$

$$\overset{++}{Pb} + 4\overset{-}{OH} = PbO_2 + 2H_2O,$$

$$4\overset{+}{H} + 2\overset{--}{SO_4} = 2H_2SO_4.$$

The process of charging is therefore just the reverse of that of discharging. That is, the theory of Le Blanc represents the accumulator as a perfectly reversible element; this is the essential difference between Le Blanc's theory and the previously given conception of Elbs. In the purely chemical relation, of course, this explanation of the changes in the lead accumulator by means of the ionic theory, as well as the following one of Liebenow, is completely identical with our fundamental equation (1).

The existence of tetravalent lead in acid solution has repeatedly been demonstrated. In 1893 H. Friedrich found that the chloride of tetravalent lead ($PbCl_4$) (therefore also tetravalent lead ions) is formed when lead peroxide is introduced into concentrated hydrochloric acid. Then in 1896

Elbs showed that, by electrolysis under suitable conditions, lead tetracetate is formed from lead diacetate. Soon after this Foerster [1] succeeded in preparing electrolytically lead tetrachloride and its ammonium double salt from lead chloride. There can be no doubt, then, that by the electrolysis of lead sulphate solutions tetravalent ions are also capable of forming and that lead peroxide in contact with dilute sulphuric acid can split off such ions.

Theory of Liebenow.

In 1896 Liebenow [2] developed a theory differing from the above in regard to the action at the peroxide electrode. He begins with the assumption that in a lead sulphate solution we must have present in addition to $\overset{++}{Pb}$ and $\overset{--}{SO_4}$ ions also bivalent negatively charged $\overset{--}{PbO_2}$, in that the $\overset{++}{Pb}$ ions will unite to a certain extent with the $\overset{--}{O}$ ions of the water to form $\overset{--}{PbO_2}$ ions. The peroxide electrode is to be considered a reversible electrode with respect to the $\overset{--}{PbO_2}$ ions, just as, for example, zinc in zinc sulphate represents a reversible electrode with respect to the zinc ions. Then during discharge the following actions take place: At the positive electrode lead peroxide passes into solution as $\overset{--}{PbO_2}$

[1] Zeitschr. f. Elektrochem. III, p. 525. 1897.
[2] *Ibid.* II, pp. 420 and 653. 1896.

ions. Since, however, this solution is saturated with $\overset{--}{PbO_2}$ ions, these react with the $\overset{+}{H}$ ions of the acid, forming $\overset{--}{Pb}$ ions and water according to the equation

$$\overset{--}{PbO_2} + 4\overset{+}{H} = \overset{++}{Pb} + 2H_2O.$$

Thereupon the lead ions combine with the $\overset{--}{SO_4}$ ions of the acid to solid sulphate:

$$\overset{++}{Pb} + \overset{--}{SO_4} = PbSO_{4\,\text{solid.}}$$

The change at the negative electrode is the same as in the case of Le Blanc's theory and consists in a passing of lead into the ionic condition.

During charging we have the reverse, i.e., at the negative pole the $\overset{++}{Pb}$ ions, and at the positive pole the $\overset{--}{PbO_2}$ ions are precipitated from the solution. As the ions are consumed, they are replaced by the sulphate accumulated at the electrodes; the $\overset{++}{Pb}$ ions by direct dissociation of the sulphate and the $\overset{--}{PbO_2}$ ions by hydrolysis:

$$\overset{++}{Pb} + 2H_2O = \overset{--}{PbO_2} + 4\overset{+}{H},$$

or, written in simpler form,

$$\overset{++}{P} + 2\overset{--}{O} = \overset{--}{PbO_2}.$$

In order to furnish this theory with a substantial foundation it is necessary to prove the existence of $\overline{\overline{PbO_2}}$ ions. This proof has also been given by Liebenow and Strasser.[1] For this purpose they electrolyzed sodium hydroxide saturated with lead hydroxide and observed that the lead contained in the anodic liquid had greatly increased after the electrolysis, showing that the lead must have wandered as anion against the positive current, i.e., the sodium plumbite must be dissociated according to the equation

$$Na_2PbO_2 = 2\overset{+}{N}a + \overline{\overline{PbO_2}},$$

wherewith the existence of $\overline{\overline{PbO_2}}$ ions is proven. This demonstration, it is true, is only for alkaline and not for dilute sulphuric aci solution. For this reason many opponents of the theory have maintained that $\overline{\overline{PbO_2}}$ ions are not capable of existing in acid solution.

However, according to the modern theory of solution there is no qualitative but only a quantitative difference between an acid and an alkaline solution. An acid differs only from an alkaline solution in that the former contains more $\overset{+}{H}$ ions and less $\overline{OH}$ ions than the latter. Therefore all ions which occur in an alkaline solution must also be capable of existing up to a certain concentration (even if frequently a very small one in an acid

[1] Zeitschr. f. Elektrochem. II, p. 653. 1896.

solution. Consequently one must concede the presence of $\overline{\overline{PbO_2}}$ ions in dilute sulphuric acid which contains lead salts; it is in fact easily possible to directly calculate the concentration of $\overline{\overline{PbO_2}}$ ions in sulphuric acid containing lead sulphate. For this purpose it is only necessary to know the concentration of the peroxide ions in dilute sodium hydroxide, i.e., the solubility of lead hydroxide in sodium hydroxide.

Two determinations which I carried out for this purpose gave for 0.066 normal alkali at 24° C. an average concentration of 0.00305 g.-mol. Na_2PbO_2 to the liter. Since such a calculation of ion concentration can at best be carried out with only a certain rough approximation, we will assume that the sodium plumbite is completely dissociated. The concentration of the $\overline{\overline{PbO_2}}$ ions can then at most be 0.003 g.-mol. per liter. The corresponding concentration of the alkali (hydroxyl ions) is, after subtracting the amount consumed in the formation of the plumbite, equal to 0.054 g.-mol. per liter.

Now we can think of the peroxide ions, as has previously been mentioned, as formed by the reaction of lead ions with the oxygen ions of the water:

$$\overset{++}{Pb} + 2\overline{\overline{O}} = \overline{\overline{PbO_2}}.$$

The $\overline{\overline{O}}$ ions are formed from water according to the equation

$$H_2O = 2\overset{+}{H} + \overline{\overline{O}}.$$

Applying the law of chemical mass action to the last two reactions, indicating ion concentrations by the chemical symbols enclosed in brackets, we get

$$\left[\overset{--}{PbO_2}\right] = \text{const.} \left[\overset{++}{Pb}\right] \cdot \left[\overset{--}{O}\right]^2,$$

$$\left[\overset{--}{O}\right] = \frac{\text{const.}}{\left[\overset{+}{H}\right]^2},$$

from which follows:

$$\left[\overset{--}{PbO_2}\right] = \text{const.} \frac{\left[\overset{++}{Pb}\right]}{\left[\overset{+}{H}\right]^4} \quad . \quad . \quad . \quad (11)$$

The concentration of the $\overset{--}{PbO_2}$ ions is therefore proportional to the first power of the concentration of lead ions and inversely proportional to the fourth power of the concentration of the hydrogen ion (acid concentration).

Now the concentration of $\overset{+}{H}$ ions in the above alkali is calculated from Kohlrausch and Heydweiller's constants for the first step of water dissociation,

$$\left[\overset{+}{H}\right] \cdot \left[\overset{-}{OH}\right] = 1.1 \times 10^{-14} \ (24^\circ \text{ C.}),$$

to be 2.2×10^{-13}, when we introduce for $[\overset{-}{OH}]$ the value for a dissociation of 90 per cent of the 0.05 alkali. The solubility of lead hydroxide in pure water is, according to the conductivity meas-

urements of Kohlrausch and Rose,[1] 4×10^{-4} g.-mol. per liter. We have therefore, approximately, $\left[\overset{++}{\mathrm{Pb}}\right] \cdot \left[\overset{-}{\mathrm{OH}}\right]^2 = (4 \times 10^{-4})^3 = \text{about } 0.64 \times 10^{-10}$, and for 0.05 normal alkali

$$\left[\overset{++}{\mathrm{Pb}}\right] = \frac{0.6 \times 10^{-10}}{\left[\overset{-}{\mathrm{OH}}\right]^2} = \text{about } 2 \times 10^{-8}.$$

From the given values for $\left[\overset{++}{\mathrm{Pb}}\right]$, $\left[\overset{-}{\mathrm{H}}\right]$, and $\left[\overset{--}{\mathrm{PbO_2}}\right]$ the proportionality factor is calculated to be 0.3×10^{-45}, so that we get for calculating the concentration of peroxide ions the equation

$$\left[\overset{--}{\mathrm{PbO_2}}\right] = 0.3 \times 10^{-45} \frac{\left[\overset{++}{\mathrm{Pb}}\right]}{\left[\overset{+}{\mathrm{H}}\right]^4}. \quad . \quad . \quad (12)$$

Therefore a solution normal with respect to lead salt and acid has the very small peroxide ion concentration of 10^{-45} g.-mol. per liter. In sulphuric acid solution it is considerably less on account of the slight solubility of lead sulphate. For example, for 0.1 molecular acid we have to take $\left[\overset{+}{\mathrm{H}}\right] = 0.2$.

The solubility of lead sulphate in water is, according to Fresenius [2] as well as Kohlrausch and Rose,[1] 1.4×10^{-4} g.-mol. per liter. Assuming com-

[1] Wied. Ann. 50, p. 135. 1893.
[2] Lieb. Ann. 59, p. 125.

plete dissociation, the law of mass action gives, therefore,

$$\left[\overset{++}{Pb}\right] \cdot \left[\overset{--}{SO_4}\right] = (1.4 \times 10^{-4})^2 = 2 \times 10^{-8}.$$

In above sulphuric acid $\left[\overset{--}{SO_4}\right]$ = about 0.1, and consequently

$$\left[\overset{++}{Pb}\right] = \text{about } 2 \times 10^{-7}.$$

Equation (12) finally gives

$$\left[\overset{--}{PbO_2}\right] = \text{about } 4 \times 10^{-50} \text{ g.-mol. per liter.}$$

As Nernst [1] has pointed out, there is, however, no ground for this small concentration not being active electromotively; for are not silver ions separated quantitatively, even with large current densities, from a potassium silver cyanide solution, in spite of the fact that only very few silver ions are present in the same? It is true the ions present in the immediate vicinity of the electrode would very soon be exhausted if, after the precipitation, new $\overset{--}{PbO_2}$ ions were not formed from the sulphate accumulated at the electrode.

Besides, the concentration of the $\overset{++}{Pb}$ ions lying at the basis of Le Blanc's theory is extremely small. This follows from the fact that dilute sulphuric acid which has been in contact with lead peroxide and therefore is saturated with

[1] Zeitschr. f. Elektrochem. VI, p. 46. 1899.

$\overset{++}{Pb}$ ions has acquired thereby no detectable oxidizing power, as would have to be the case if appreciable quantities of $\overset{++}{Pb}$ ions had gone into solution.

Finally, be it also mentioned that the property of good metallic conductivity of lead peroxide decidedly indicates that it can pass directly into an electrolyte as an ion.

Let us now apply Nernst's formula, as developed above, according to Liebenow's theory. Indicating the solution tension of the peroxide electrode for $\overset{--}{PbO_2}$ ions by C_0, that of the lead-sponge electrode for $\overset{++}{Pb}$ ions by C_p, and the ion concentrations in the acid by the chemical symbols in brackets, the potential difference of the peroxide electrode against the acids is given by

$$\varepsilon_0 = -\frac{RT}{2} ln \frac{C_0}{\left[\overset{--}{PbO_2}\right]} *,$$

and that of the lead electrode by

$$\varepsilon_p = \frac{RT}{2} ln \frac{C_p}{\left[\overset{++}{Pb}\right]},$$

---

* Since the peroxide electrode sends negatively charged ions into the solution, this potential difference is to be introduced into the calculation as negative.

The total electromotive force of the accumulator is then given by the difference of the single potentials:

$$E = \varepsilon_p - \varepsilon_0 = \frac{RT}{2} ln \frac{C_p \cdot C_0}{[\overset{++}{Pb}][\overset{--}{PbO_2}]}, \quad . \quad . \quad (13)$$

or, for room temperature ($T = 273 + 18$) and Briggs' logarithms,

$$E = 0.0288 \log^{10} \frac{C_0 \cdot C_p}{[\overset{--}{PbO_2}][\overset{++}{Pb}]}. \quad . \quad . \quad . \quad (14)$$

The solution tensions C_0 and C_p are constant magnitudes for a given temperature. We can therefore take as a direct result from the equation that the electromotive force E must diminish with increase in concentration of the $\overset{--}{PbO_2}$ and $\overset{++}{Pb}$ ions. In alkaline solution, when, as we saw above, many $\overset{--}{PbO_2}$ ions are present, E must accordingly be considerably smaller than in sulphuric acid; likewise in solutions of easily soluble lead salts which contain many $\overset{++}{Pb}$ ions. In fact the electromotive force of the accumulator in sodium hydroxide saturated with lead hydroxide is only about 0.8 volt; similarly, the same is considerably less in acidified lead nitrate solution than in sulphuric acid. If, on the other hand, we reduce the concentration of the $\overset{++}{Pb}$ ions and therefore, according to equation (11), also the concentration of the

PbO_2^{--} ions, the electromotive force must rise. This case could possibly be realized by precipitating the sulphate by means of hydrogen sulphide.

In the following chapter we will become acquainted with a quantitative application of the osmotic theory.

IV.

VARIATION OF ELECTROMOTIVE FORCE WITH ACID CONCENTRATION.

(*a*) *General Relations.*

Planté had already observed that the electromotive force of his secondary element rose somewhat with the concentration of the sulphuric acid. More accurate measurements covering a greater range of concentration were, however, first made by Heim.[1]

The acid concentration of a Tudor cell was gradually increased by steps of about 5 per cent. The cell was charged and discharged a number of times, and fifteen to eighteen hours after the last charging, when the excess voltage ("Ueberspannung") had disappeared, both the electromotive force and acid density were measured (at about 15° C.). The results are given in Fig. 3. The electromotive force rises almost exactly proportional to the acid concentration.

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[1] Elektrotechn. Zeitschr. X, H. 4. 1889.

A further detailed investigation of the influence of the acid density upon the E.M.F. we owe to F. Streintz.[1] Like Heim he used Tudor accumu-

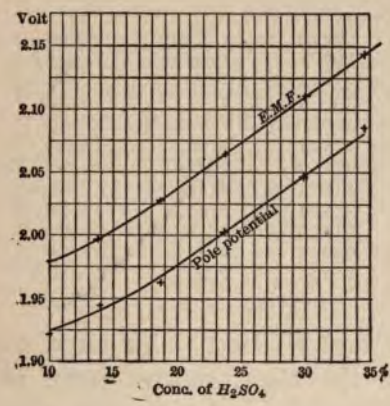

FIG. 3.

lators for the measurements. The results of this investigation are given in Table III, z indicating acid concentration in grams per liter, and E_z the electromotive force. The values of E are likewise a linear function of the acid concentration, as the agreement with the values calculated from the equation

$$E_z = 1.850 + 0.00057 \cdot z \quad . \quad . \quad . \quad (15)$$

shows.

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[1] Wied. Ann. 46, p. 449. 1892.

TABLE III.

s	E_s	
	Found.	Calculated.
86.3	1.900	1.899
166.1	1.950	1.945
236.7	1.987	1.985
296.9	2.021	2.019
366.3	2.055	2.059
425.2	2.087	2.092
470.0	2.116	2.118
516.3	2.149	2.144
570.4	2.173	2.175
611.6	2.195	2.199
640.9	2.217	2.215
684.2	2.235	2.240

Gladstone and Hibbert [1] also have made measurements of the electromotive force at different acid concentrations and obtained the following values:

TABLE IV.

Density.	Per Cent H_2SO_4.	Electromotive Force.
1.045	6.5	1.887
1.065	9.5	1.898
1.080	11.5	1.915
1.115	16.2	1.943
1.157	21.7	1.978
1.217	29.2	2.048
1.254	33.7	2.088
1.335	43.0	2.170

Comparing the measurements of Heim, Streintz, Gladstone and Hibbert, we find that they agree

[1] Elektrotechn. Zeitschr. 13, p. 436. 1892.

very well as to their relative course; the above values, however, show a marked discrepancy. This can partly be explained by the differences in the observation temperature, but most of it can only be due to errors in calibrating the measuring instruments used or to impurities in the acid.

I constructed a cell from chemically pure substances and obtained the following values by comparison with a Weston standard cell. The electromotive force of the Weston standard cell was assumed to be 1.0220 volts (15° C.).

TABLE V.

Density.	Per Cent H_2SO_4.	Electromotive Force (15° C.).
1.050	7.37	1.906
1.150	20.91	2.010
1.200	27.32	2.051
1.300	39.19	2.142
1.400	50.11	2.233

The electromotive forces are somewhat greater than those calculated from Streintz's equation (15); however the variations are mostly less than 1 per cent.

Let us now attempt to account theoretically for the rise of the electromotive force with the increase in acid density, by first making use of a simple thermodynamical cycle.[1] For this purpose

[1] Zeitschr. f. Elektrochem. IV, H. 15. 1897/98, and Wied. Ann. 65, p. 894. 1898.

let us imagine two accumulators charged with sulphuric acid of different concentration, so connected (like poles with each other) that their electromotive forces oppose each other, and furthermore let accumulator I be filled with acid more concentrated than that of accumulator II. Since the electromotive force of I is greater than II, we can remove electrical energy from this system, whereby accumulator I is discharged and accumulator II is charged. The consumption of the solid substances PbO_2, Pb, and $PbSO_4$ in the one accumulator is completely covered by the formation of an equal amount of the same substances in the other accumulator, and we have as the current-producing process the transference of H_2SO_4 from the more concentrated solution in I into the more dilute in II, and of H_2O from II to I. By the removal of 96540 coulombs, which corresponds to the decomposition of 1 g.-equivalent, the change in the free energy amounts to

$$W = \Delta E \; 96540 \text{ volt-coulombs},$$

where ΔE stands for the difference between the electromotive force of I and II.

The computation of W can be carried out in two other independent ways: first, by using the heat effect which accompanies the transference of sulphuric acid and water, and the temperature coefficient of ΔE; second, by isothermal distillation, in that we apply to the accumulator

the calculation developed by H. v. Helmholtz for the dependence of the electromotive force of the calomel element upon the concentration of its solution. On account of the importance which these calculations possess for the theory of the accumulator, it will be well to follow up both methods.

The heat of dilution of sulphuric acid has been measured by J. Thomsen;[1] it follows from the empirical formula given by him that the heat developed by mixing a g.-mol. H_2SO_4 with b g.-mol. H_2O is given by

$$H = \frac{a \,.\, b}{b + 1.798a} + 17860 \text{ cal.}$$

It is evident that the heat development accompanying the transference of sulphuric acid from accumulator I to II is given by the difference between the heat of admixture of sulphuric acid to the solution in I and to the solution in II, and that the heat effect corresponding to a transference of water is given by the difference of the heat of admixture of water to the solution in I and the solution in II.

The heat of admixture of $1H_2SO_4$ or $1H_2O$ to a large quantity of a sulphuric acid solution of a g.-mol. H_2SO_4 and b g.-mol. H_2O is given by the partial differential quotient of H with respect

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[1] Thermochem. Untersuchungen III, p. 54.

to a and b. Indicating the former by U and the latter by U', we have

$$U' = \frac{\partial H}{\partial a} = \frac{17860b^2}{(b+1.798a)^2} \text{ cal.}, \quad . \quad . \quad . \quad (16)$$

$$U = \frac{\partial W}{\partial b} = \frac{1.798a^2}{(b+1.798a)^2} 17860 \text{ cal.} \quad . \quad (17)$$

The change in the total energy (heat effect) Q, corresponding to the current-giving process of our system, which consists of two accumulators arranged opposing each other, is, therefore,

$$Q = U_{II} - U_I + U_I' - U_{II}'.$$

The indices I and II indicate the values of the two accumulators.

Now according to the second law of the theory of heat in Helmholtzian form, we have the well-known relation (p. 25) between the change of the free energy W of a reaction, its temperature coefficient $\frac{\partial W}{\partial T}$, and the heat effect Q,

$$W = Q + T\frac{\partial W}{\partial T}.$$

Remembering that

$$W = 96540\ \Delta E \text{ volt-coulombs},$$

and 1 volt-coulomb is equivalent to 0.239 g.-cal., we get

$$\Delta E = \frac{Q}{23073} + T\frac{\partial \Delta E}{\partial T} \text{ volts.} \quad . \quad . \quad .(18)$$

or, using Briggs's logarithms,

$$\Delta E = 1.983 \times 10^{-4} T \left(n_2 \log p_2 + \log \frac{p_2}{p_1} - n_1 \log p_1 - \int_{n_1}^{n_2} \log p \, dn \right). \quad (20)$$

Thanks to the efforts of Dieterici,[1] we are in possession of extremely exact measurements of the vapor pressure of sulphuric acid solutions, and have therefore also in this case all data for the calculation of ΔE.

In order to test by experiment the two equations for ΔE, I introduced into melting ice a cell constructed of pure lead oxide charged with various solutions of sulphuric acid, and measured the accompanying electromotive forces. The results are contained in Table VI. The values for the water-vapor pressure p are taken from the measurements of Dieterici, likewise carried out at 0° C.

The calculated values for the electromotive force were obtained by computing the differences between E and the value of III (2.103 volts) by means of equations (18) and (20), and then adding the same to III.

In order to also test equations (18) and (20) on a technical accumulator, I took the same differences, in as far as the statements of temperature, temperature coefficient, etc., permitted it, from the measurements of Heim and Streintz made

[1] Dieterici, Wied. Ann. 50, p. 61. 1893.

upon a Tudor accumulator, and introduced the values of E thus obtained into the table.

TABLE VI.

Number.	Acid Density, 15° C.	Per Cent H_2SO_4.	n	Vapor-pressure p, mm. Hg.	$\frac{\partial E}{\partial T}$ Millivolts.	Electromotive Force E (0° C.), Volts.				
						Calculated.		Found.		
						From Q.	From p.	Author.	Streintz.	Heim.
I	1.553	64.5	3	0.431	+0.04	2.39	2.383	2.355	—	—
II	1.420	52.15	5	1.297	+0.06	2.25	2.257	2.253	2.268	—
III	1.266	35.26	10	2.975	+0.11	(2.10)	(2.103)	2.103	(2.103)	(2.103)
IV	1.154	21.40	20	4.027	+0.32	2.06	2.000	2.008	1.992	2.002
V	1.035	5.16	100	4.540	−0.07	1.85	1.892	1.887	1.891	—

As the figures show, the agreement between calculated and measured values is excellent.

The values calculated from Q are (especially in the case of the more dilute solutions IV and V) less exact, since they are derived from an equation conforming only imperfectly to the facts. The value of the member $T\left(\frac{\partial E}{\partial T}\right)$ in equation (18) is taken from the measurements of Streintz [1] on the temperature coefficient. This could be done with sufficient accuracy, since the maximum value of this member amounted to only 0.05 volt. The small temperature coefficient of our system is also in good agreement with the fact established by Nernst,[2] that the change of the free energy,

[1] Streintz, Wied. Ann. 46, p. 454. 1892.

[2] Nernst, *Ibid.* 53, p. 57. 1894.

upon mixing sulphuric acid solutions, very nearly agrees with the change of the total energy (heat effect) of this process. The measurements of Heim and Streintz, given in Table VI, show that the equations (18) and (20) also hold good for the forms of the accumulator used in actual practice.

The fact that the two above calculations, carried out by independent methods, agree so well with the experiment, along with the mentioned results of the thermochemical investigation of Streintz and Tscheltzow, certainly proves most conclusively that the current-giving process in the accumulator can only be expressed by equation (1) and no other; not excluding, of course, the reversible formation and disappearance of intermediate products.

The above calculations give an important hint toward achieving a higher electromotive force in the construction of practical accumulators. Every addition to the accumulator acid which reduces the water-vapor pressure of the same and does not disturb the electrolytic process must increase the electromotive force. However, it seems difficult to find an indifferent substance which can for a considerable time resist the oxidizing action of the PbO_2 and the reducing action of the lead sponge. The substance added must at the same time not appreciably influence the conductivit , for then, as will be shown below, the efficiency must be considerably lowered. The

use of very concentrated sulphuric acid is out of the question on account of its directly attacking the lead sponge. By the amalgamation of the lead this action can be very considerably reduced and electromotive forces obtained of over 2.7 volts, but only for a short time. It may be well to mention that, on the basis of the above calculation and measurements, the lead accumulator represents a very convenient apparatus for the determination of the change in free energy produced by mixing sulphuric acid solutions. Therefore the tables for the variation of the electromotive force with the acid concentration are at the same time to be considered as tables showing the change in free energy with the change in concentration of a sulphuric acid solution.

(*b*) *Relations for Dilute Solutions.*

Equation (20), which expresses the relation between the vapor pressure of the acid and the electromotive force of the accumulator, is unwieldy for practical purposes and possesses, therefore, only theoretical interest. If, however, we do not take into consideration all concentrations, but only dilute sulphuric acid solutions, say from about twice normal down, then the same takes a very simple form. Imagine, for instance, the two accumulators filled with acids which differ in their concentrations by an infinitesimal amount;

then, putting $n_2 = n_1 + \partial n$, $p_2 = p_1 + \partial p$, the above equation passes into the form

$$\frac{\partial E}{\partial n} = -RT(n+1)\frac{\partial ln p}{\partial n}. \quad . \quad . \quad . \quad (21)$$

If we introduce into this equation, in place of n, the normal concentration c (g.-mol. per liter), we obtain for the acid coefficient of the accumulator, since in dilute solution $n = \frac{55.5}{c}$, the relation

$$\frac{\partial E}{\partial c} = -\ 5.5RT\left(\frac{1}{c} + 0.018\right)\frac{\partial ln p}{\partial c}.$$

Now $-\frac{\partial ln p}{\partial c} = -\frac{\partial p}{p} \cdot \frac{1}{\partial c}$ is the relative depression of the vapor-pressure upon the addition of 1 g.-mol. H_2SO_4, and this is, according to the Raoult-van't Hoff law, independent of the concentration and has for electrolytes, which by dissociation decompose into ν parts, the value $\frac{\nu}{N}$, N indicating the g.-mol. of water contained in one liter ($N = 55.55$). The acid cofficient therefore becomes

$$\frac{\partial E}{\partial c} = \nu RT\left(\frac{1}{c} + 0.018\right). \quad . \quad . \quad . \quad (22)$$

The integration of this equation from c_1 to c_2 finally gives, after introducing the value of R and using Briggs's logarithms,

$$E_2 - E_1 = 0.1983 \times 10^{-3} \nu T\left(\log^{10}\frac{c_2}{c_1} + 0.008[c_2 - c_1]\right) (23)$$

Since sulphuric acid separates into three parts by dissociation, ν would here be equal to 3. Sulphuric acid of normal concentration is, however, as the freezing-point determinations have shown, only partially dissociated, and ν has therefore in reality a value less than 3.

According to the measurements given below, and the freezing-point determinations of dilute sulphuric acid solutions by Loomis, both of which are in good agreement, ν from normal acid down has the mean value of 2.22 at 0° C. The E.M.F. of the accumulator, charged with acid of normal concentration, as given by a number of measurements, agreeing to within 0.0002 volt, is 1.917 volts at 0° C.[1]

Introducing this value into equation (23), we get for the E.M.F. E_c at the acid concentration c and 0° C.

$$E_c = 1.917 + 0.120 \log^{10} c + 0.001 c, \quad . \quad . \quad (24)$$

and for room temperature (18° C.) approximately

$$E_c = 1.92 + 0.15 \log^{10} \cdot c. \quad . \quad . \quad . \quad . \quad . \quad (25)$$

These equations permit the calculation of the E.M.F. in a very simple manner, from the concentration of the acid. They are a special case of the general equation (20), and are applicable for acids which are more dilute than twice normal,

[1] 1.0220 volts at 15° C. was the E.M.F. of the Normal Weston element assumed.

with the one condition that the reduction of the vapor-pressure produced by the dissolved lead sulphate be negligible as compared with the change in vapor-pressure caused by the acid. The equation therefore holds good only down to about 0.0005 normal acid.

Of course we arrive at the ame relationship when we consider the interdependence of the E.M.F. of the accumulator and the acid concentration, in accordance with Nernst's (osmotic) theory of the galvanic cell. Since the laws of osmotic pressure are true only for dilute solutions, the theory does not give equation (20), but only the one for dilute solutions. We arrive at the same, however, by a much shorter and simpler course.

The following is the derivation of equation (23) from the standpoint of the peroxide-ion theory developed by Liebenow. It is especially to be noted, however, that the theory of Le Blanc leads to the same equation.

According to Liebenow's theory the E.M.F. of the accumulator, as we have seen on p. 49, is determined by the solution pressure of the peroxide and lead electrodes (C_0) and (C_p), and the concentration of the peroxide and lead ions ($[\overset{--}{PbO_2}]$ and $[\overset{++}{Pb}]$), and is given by the equation

$$E = \frac{RT}{2} ln \frac{C_p \cdot C_0}{[\overset{++}{Pb}][\overset{--}{PbO_2}]}.$$

The concentration of the peroxide ions is given (p. 46) by the concentration of the hydrogen ions according to the equation[1]

$$\left[\overset{--}{PbO_2}\right] = \text{const.} \frac{\left[\overset{++}{Pb}\right]\left[H_2O\right]^2}{\left[\overset{+}{H}\right]^4}.$$

Since solid lead sulphate is always present in the accumulator, we have, according to Nernst's law of solubility reduction, the product of $\overset{++}{Pb}$ and $\overset{--}{SO_4}$ ions constant:

$$\left[\overset{++}{Pb}\right] \cdot \left[\overset{--}{SO_4}\right] = \text{const.}$$

If, further, we consider that, on account of the slight solubility of lead sulphate, $\left[\overset{--}{SO_4}\right] = \frac{\left[\overset{+}{H}\right]}{2} = c$, and indicate the active mass of the water (H_2O) by c_0, it follows that

$$\left[\overset{++}{Pb}\right] \cdot \left[\overset{--}{PbO_2}\right] = \frac{c_0^{\,2}}{c^6} \cdot \text{const.},$$

$$E = \frac{RT}{2} ln \frac{C_p \cdot C_0 \cdot c^6}{C_0^{\,2}} \cdot \text{const.}$$

Wherewith we obtain for the difference between the electromotive forces of two accumulators with the acid concentrations c_1 and c_2:

$$E_2 - E_1 = \frac{RT}{2} ln \frac{c_2^{\,6} c_{0_1}^{\,2}}{c_1^{\,6} c_{0_2}^{\,2}}. \quad . \quad . \quad . \quad (26)$$

[1] In the calculations on p. 46 the active mass of the water (H_2O) could be considered constant. In the above more accurate calculations, however, its variation cannot be ignored.

The active mass c_0 of the water is proportional to the vapor-pressure p; therefore we can substitute $\frac{p_1}{p_2}$ for $\frac{c_{0_1}}{c_{0_2}}$.

For dilute solutions, however, the reduction of the vapor-pressure by the substance dissolved is small as compared with the absolute value of p and therefore

$$ln\frac{p_1}{p_2}=\frac{p_2-p_1}{p_2}=\frac{3(c_2-c_1)}{N}.$$

Substituting this in above equation, the same becomes identical with (23) and (24).

In conclusion be it mentioned that the direct application of the law of mass action to the chemical equation of the action in the accumulator leads at once to the same relation. For very dilute acid we can assume complete dissociation of the sulphuric acid and lead sulphate and therefore write our reaction equation in the form

$$PbO_2+Pb+4\overset{+}{H}=2\overset{++}{Pb}+2H_2O.$$

Since PbO_2 and Pb are present in solid form and consequently their active masses are constant, the law of mass action gives

$$\frac{\left[\overset{+}{H}\right]^4}{\left[\overset{++}{Pb}\right]^2\cdot\left[H_2O\right]^2}=\text{const.}=\text{const.}\cdot K,$$

K indicating the equilibrium constant of above reaction. The van't Hoff expression for the re-

lation between E.M.F. and chemical equilibrium is

$$E = \frac{RT}{2} lnK, \quad . \quad . \quad . \quad . \quad . \quad (27)$$

giving equation (26), etc., dircetly.

In order to experimentally test equation (24), I built two small accumulators out of pure lead oxide and placed the same in a water-bath surrounded by melting ice. The one was kept filled with normal acid, while the other was successively charged with acid from 0.4 down to 0.0004 normal. The difference of the electromotive forces of the two accumulators was measured by compensation.

The following table contains the results of the measurements:[1]

TABLE VII.

Gram-mol. H_2SO_4 per Liter, c.	Electromotive Force (0° C.), E_c.	
	Found.	Calculated.
1.000	1.917	(1.917)
0.360	1.863	1.863
0.180	1.828	1.827
0.111	1.802	1.801
0.0505	1.764	1.760
0.0124	1.690	1.687
0.00046	1.488	1.516

[1] Based on the Normal Weston element, whose E.M.F. was taken as 1.0220 volts at 15° C.

The third column gives the values for E as calculated by means of equation (24). The difference between the measured and calculated values are exceedingly small and lie well within the range of experimental error; only in the case of the last value does it reach 2 per cent, because here the dissociation of the acid has advanced to a very marked extent and hence the value introduced for ν should be greater than 2.22.

As demanded by the theory, the E.M.F. falls off rapidly with the dilution of the acid.

If we should reduce the concentration of the acid considerably below 0.0004, according to the above expression, the E.M.F. would have to become zero, and finally even change its direction, i.e., its algebraic sign. Practically, however, this limit case cannot be realized, because the dissolved lead sulphate is partially broken up hydrolytically into lead hydroxide and sulphuric acid. As has been mentioned, equations (24) and (25) hold good only down to about 0.0005 normal acid; for more dilute acids the assumption that $\left[\overset{--}{SO_4}\right] = \frac{\left[\overset{+}{H}\right]}{2} = c$ is not true, since the solubility of lead sulphate equals 0.00013 g.-mol. per liter. From this acid concentration down we have, therefore, to calculate with the equation

$$E = \frac{RT}{2} ln \frac{C_p \cdot C_0 \left[\overset{+}{H}\right]^4}{\left[\overset{++}{Pb}\right]^2}, \quad . \quad . \quad . \quad (28)$$

which follows directly from equation (11). For the difference between the electromotive forces of two accumulators with different concentrations of acid we get the equation

$$E_2 - E_1 = RT\ln\frac{\left[\overset{++}{\mathrm{Pb}}\right]_1}{\left[\overset{++}{\mathrm{Pb}}\right]_2} + RT\ln\frac{\left[\overset{+}{\mathrm{H}}\right]_2^2}{\left[\overset{+}{\mathrm{H}}\right]_1^2}. \quad . \quad (29)$$

In order to give an application of the above expression, we will employ it to calculate the concentration of sulphuric acid in a pure lead sulphate solution, i.e., the degree of hydrolytic dissociation of lead sulphate. A knowledge of this is of significance as regards the question of the constitution of lead salts in solution, and consequently also the theory of the lead accumulator. All that is necessary is to determine the E.M.F. of the accumulator filled with pure lead sulphate solution. Actual measurement gave 1.26 volts (E_1) at 0° C.

Now the solubility of lead sulphate at 0° C., according to the closely agreeing conductivity measurements of Kohlrausch and Rose [1] and the analytical determinations of Fresenius,[2] is 41 mg. $= 1.3 \cdot 10^{-4}$ mol. per liter. Therefore $\left[\overset{++}{\mathrm{Pb}}\right]_1 = 1.3 \cdot 10^{-4}$. If, in addition, we introduce from

[1] Wied. Ann. 50, 135. 1893.
[2] Lieb. Ann. 59, p. 125.

Table VII $E_2 = 1.488$ and $\left[\overset{+}{H}\right]_2 = 2 \times 0.00046$, it follows that

$$\left[\overset{+}{H}\right]_1 = 3 \times 10^{-5},$$

from which we get the hydrolysis of lead sulphate at 0° C. to be from 5 to 10 per cent. Unfortunately, up to the present no direct determination of the hydrolytic decomposition of lead sulphate has been made. Ley [1] recently found for a 0.01 *n*-solution of lead chloride, an hydrolysis of 0.6 per cent at 100° C.

If we reduce the acid concentration in the accumulator beyond the amount corresponding to the hydrolytic decomposition of the lead sulphate, the possibility of sulphate formation ceases, and we have in its place a reduction of the peroxide and an oxidation of the lead sponge to lead hydroxide according to the equation

$$PbO_2 + Pb + 2H_2O = 2Pb(OH)_2.$$

The free energy of this reaction is given by the E.M.F. of the accumulator, when the same is filled, not with acid, but with dilute sodium hydroxide saturated with lead oxide. Measurements give a value of 0.8 volt.

Of the E.M.F. of the accumulator, then, 40 per cent (0.8 volt) is due to the reduction of peroxide

[1] **Zeitschr.** physikal. Chem. 30, p. 193. 1899.

and the oxidation of lead sponge, 20 per cent (0.4 volt) to the change of oxide into sulphate, and 40 per cent (0.8 volt), almost one half, to a sulphuric acid concentration chain, i.e., as a result of the fact that diluting sulphuric acid is accompanied by such a great change in energy.

V.

VARIATION OF ELECTRODE POTENTIAL WITH ACID CONCENTRATION.

(*a*) *General Relations.*

In the preceding chapter the variation of the E.M.F. of the lead accumulator for the entire accessible range of concentration was considered. Now the question arises, how does this change distribute itself with regard to the potential at the separate electrodes? We have on this point an investigation by Streintz.[1] He determined the potential difference of the accumulator electrodes, with varying acid strength, as against a zinc electrode placed in a porous cup containing a concentrated solution of zinc sulphate. He found that, as measured against the electrode, the potential of the peroxide electrode rises with the concentration of the acid, while that of the lead electrode diminishes. Let P_s stand for the potential of the peroxide electrode against the zinc electrode, p_s for that of the lead-sponge elec-

[1] Wied. Ann. 49, p. 546. 1893.

trode against zinc, s for the density of the acid, and s_0 for the density of pure water at the temperature of observation; then the measurements of Streintz may be expressed by the empirical formulæ

$$P_s = 2.3275 + 0.5925(s - s_0),$$
$$p_s = 0.4775 - 0.3245(s - s_0).$$

In this arrangement, however, potential differences develop at the points of contact between zinc sulphate solution and sulphuric acid, which cannot be calculated in the case of concentrated solutions; hence these measurements cannot be used for an exact testing of the theory. It is necessary to employ an electrode which is reversible with respect to one of the ions of the acid and so can be directly introduced into the accumulator acid. The hydrogen and mercurous sulphate electrode are of this kind.

Upon introducing a platinum foil charged with hydrogen into the accumulator, we obtain with the accumulator electrodes the two reversible galvanic combinations, PbO_2, $PbSO_4$—H_2SO_4—H_2 and Pb, $PbSO_4$—H_2SO_4—H_2, in which the following reactions take place during the production of current:

$$PbO_2 + H_2 + H_2SO_4 \rightleftarrows PbSO_4 + 2H_2O$$

and

$$Pb + H_2SO_4 \rightleftarrows H_2 + PbSO_4.$$

Since $PbSO_4$ is present in solid form and the acid therefore is kept saturated with this salt, the change in the liquid phase of both elements during discharging consists in the consumption of $1H_2SO_4$. In the PbO_2 element there are formed in addition $2H_2O$. In as far as the electromotive forces depend upon the acid concentration, they must differ by the difference in the free energy of formation of water, in sulphuric acid of varying concentrations.

This is given by the work of distilling water from the more dilute into the more concentrated acid.

If we indicate the E.M.F. of the element H_2—PbO_2 by e, and that of the element H_2—Pb by e', the water-vapor pressure of the acid by p_1 and p_2 respectively, then

$$\Delta e - \Delta e' = RTln\frac{p_2}{p_1} = 1.98 \times 10^{-4} T \log^{10}\frac{p_2}{p_1}. \qquad (30)$$

If in an analogous way, as was done (p. 59) for the accumulator, we calculate from the work of distillation the effect of the acid density upon the E.M.F. of the above combinations, we obtain two quite similar equations, whose subtraction gives equation (30). In the same way we get for the dilution coefficients the expressions

$$\frac{\partial e}{\partial n} = -\frac{RT}{2}(n+2)\frac{\partial lnp}{\partial n} \ldots (PbO_2—H_2), \qquad (31)$$

$$\frac{\partial e'}{\partial n} = -\frac{RT}{2}n\frac{\partial lnp}{\partial n} \ldots\ldots (Pb—H_2), \qquad (32)$$

from which follows

$$\frac{\partial e}{\partial n} = \frac{\partial e'}{\partial n} \cdot \frac{n+2}{n}. \quad . \quad . \quad . \quad . \quad (33)$$

As long as n is large as compared with 2, both elements change equally rapidly. For a mixture of 1 mol. sulphuric acid to 2 mol. water ($n=2$) the E.M.F. of the peroxide element changes twice, for a mixture of 1 mol. H_2SO_4 to 1 mol. water, three times as rapidly as that of the lead element.

In order to verify these equations, I determined the potentials of the single accumulator electrodes with various acid densities over and against a hydrogen electrode, consisting of a platinized platinum electrode continuously bathed with hydrogen and dipped into the same acid. As regards the details of carrying out such measurements I refer to the last chapter.

The results are contained in Table VIII.[1]

The values for p are taken from the measurements of Dieterici. The calculated values for e and e' were obtained by computing by means of equation (30) the values for Δe from the measured ones for $\Delta e'$ and p, and the values for $\Delta e'$ from the measured Δe and p values. The differences thus obtained were then added to the value of No. III.

[1] The measurements were carried out with ordinary accumulator plates; it is surmised that with entirely pure substances the values would be somewhat higher.

TABLE VIII.

No.	Acid Density, 15° C.	Per Cent H_2SO_4.	Vapor-pressure, p. 0° C. mm. Hg.	Electromotive Force 0° C.			
				PbO_2—H_2. e		Pb—H_2. e'	
				Found.	Calc.	Found.	Calc.
I	1.033	4.86	4.55	1.610	1.604	0.269	0.275
II	1.064	9.33	4.45	1.617	1.617	0.282	0.282
III	1.141	19.76	4.02	1.654	(1.654)	0.317	(0.317)
IV	1.192	26.36	3.68	1.682	1.678	0.339	0.343
V	1.428	52.93	1.24	1.801	1.791	0.426	0.436

Since the electromotive forces are calculated from the second differences, errors to the extent of 0.006 volt are possible.

The variations between the calculated and measured values are almost without exception within this limit.

The relations are much simpler than in the case just considered, when we use as the measuring electrode, instead of the hydrogen, the mercurous sulphate electrode, consisting of mercury covered with mercurous sulphate. The current-producing reactions of the two galvanic combinations obtained with this electrode are

$$PbO_2 + 2Hg + 2H_2SO_4 \rightleftarrows PbSO_4 + Hg_2SO_4 + 2H_2O,$$
$$Pb + Hg_2SO_4 \rightleftarrows PbSO_4 + 2Hg.$$

The second equation shows that during current production no change takes place in the solution of the element Pb—Hg, for Hg_2SO_4 and $PbSO_4$ are present in the solid form and keep up the

saturation of these salts. The E.M.F. of this element must therefore be entirely independent of the liquid phase and consequently also of the amount of acid in the same. On the other hand, in the PbO_2—Hg element we have, as in the accumulator, $2H_2SO_4$ consumed and $2H_2O$ formed during the passing of the current. That is, the dependence of this element upon the acid concentration is the same as that of the accumulator and is determined by the same equations. The lead electrode measured against a mercurous sulphate electrode, then, appears independent, while only the peroxide electrode appears dependent, upon the acid concentration.

Several measurements in this connection showed that these demands of the theory are also very exactly fulfilled.

The following acid concentrations gave the E.M.F. standing under each:

	6.5	10.2	16.5	% H_2SO_4.
Hg—Pb	0.96	0.96	0.956	} volt (0° C.)
Hg—PbO_2	0.93	0.95	0.99	

The measurements of Streintz (l. c.) can be explained in the same simple manner. As stated, this investigator employed for a measuring electrode zinc in a saturated zinc sulphate solution. For the same reason as in the case of the mercurous sulphate solution the E.M.F. of the combination Pb—Zn would have to be independent

of the acid concentration. However, the potential difference of the liquid chain H_2SO_4 aq—$ZnSO_4$ aq which acts against the electromotive forces, increases greatly with the acid density and thereby effects a falling off of the E.M.F. of the Pb—Zn element with the acid density and a retarded increasing of the combination PbO_2—Zn.

Although the above measurements give valuable insight into the behavior of the individual accumulator electrodes with different acid densities, and we shall frequently make use of them, yet the same do not give a clear picture of the change of the potential of the accumulator electrodes with the acid alone, since the potential of the auxiliary electrodes also changes. And as we saw above, in the case of different measuring electrodes, the accumulator electrodes show in consequence an apparently very different behavior with variation in concentration. A better insight into the changes at the accumulator electrodes alone is obtained by determining the potentials of different densities of acid against the same electrode in a definite constant concentration, i.e., by using concentration chains of the form

Pb | $PbSO_4$ conc. acid—dilute acid $PbSO_4$ | Pb,

and

PbO_2 | $PbSO_4$ conc. acid—dilute acid $PbSO_4$ | PbO_2.

Chains of that kind were first investigated by

Gladstone and Hibbert,[1] and recently by Mugdan;[2] the latter also treated them theoretically. These interesting investigations pertain only to dilute acids, but since very simple and generally applicable relations can be derived for more concentrated solutions of acid, such as are used in practice in accumulators, the investigations of Mugdan will be discussed later.

When the above concentration chains give current $PbSO_4$ is consumed, H_2SO_4 and Pb or PbO_2 are formed in the dilute acid, and in the concentrated acid Pb or PbO_2 and H_2SO_4 are consumed and $PbSO_4$ is formed. In the peroxide chain we have in addition $2H_2O$ which are formed in the concentrated solution and disappear in the dilute.

The total consumption of the solid substances Pb | PbO_2 and $PbSO_4$ in the chains is therefore zero, and there remains as the current-producing action only the transportation of H_2SO_4 from the concentrated into the dilute acid. We must, however, remember that in the above chains the acid equalization does not only take place through the decomposition and formation of sulphate, but also to a large extent through electrolytic transportation at the points of contact of the acids of different concentration.

We will next consider the chain

Pb | $PbSO_4$ conc. acid—dil. acid $PbSO_4$ | Pb.

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[1] Elektrotechn. Zeitschr. 1892, p. 436.

[2] Zeitschr. f. Elektrochem. 1899, p. 316.

If we take out of the same an amount of current equal to $2F$ ($F = 96540$ coulombs), it performs the work

$$W_1 = 2F\Delta\varepsilon_1 \text{ volt-coulombs},$$

where $\Delta\varepsilon_1$ stands for the E.M.F. At the same time the current liberates 1 mol. SO_4 in the dilute acid and binds 1 mol. SO_4 in the concentrated acid. Besides 2μ H atoms migrate from the concentrated to the dilute acid and $(1-\mu)SO_4$ molecules from the dilute into the concentrated acid, μ representing the Hittorf migration number of sulphuric acid. The total amount of acid transported by the current from the concentrated to the dilute solution is, therefore,

$$1SO_4 + 2\mu H - (1-\mu)SO_4 = \mu H_2SO_4.$$

Now, as we saw above (p. 60), the migration of 1 mol. H_2SO_4 is equivalent to a distillation work

$$RT(n_2 \log p_2 - n_1 \log p_1 - \int_{n_1}^{n_2} \log p\, dn),$$

which for the sake of brevity we shall write $RTf(p)$.

The work performed by our concentration chain is therefore $RT\mu f(p)$, so that upon considering the electrical work W an E.M.F. is given:

$$\Delta\varepsilon_1 = 0.990 \times 10^{-4} T\mu f(p). \quad . \quad . \quad . \quad (34)$$

In order to test this equation we shall make use of the measurements of Gladstone and Hibbert.

Since these observations were made at room temperature, we cannot carry out the calculations for $f(p)$ by means of the vapor-pressure measurements of Dieterici used above, but are dependent upon the measurements of Regnault, which are not accurate enough, however, for the particular purpose. According to the discussion in the previous chapter we are justified in calculating $f(p)$ from the change of the E.M.F., with the acid concentration, of the entire accumulator at the particular temperature. By means of equation (20) we obtain directly

$$\Delta\varepsilon_1 = \mu\left(\frac{\Delta E}{2} - 0.0287 \log \frac{p_2}{p_1}\right). \quad . \quad . \quad (35)$$

Of course for the calculation of $\log \frac{p_2}{p_1}$ the values of Regnault are sufficiently accurate. In Table IX are placed side by side the values obtained by means of this equation and by measurement. The values for E are taken from Table IV, those for μ are exterpolated from the measurements of Hittorf. In the calculation the mean value of μ was introduced for both concentrations, and for 0.2 per cent acid the value 0.80 was used.

Since the temperature is not given in the case of Gladstone and Hibbert's measurements, the E.M.F. of the accumulator for 0.2 per cent acid, which changes greatly with the temperature, had to be calculated from the measurements themselves. The value obtained was 1.690 volts. At

higher concentrations (above 30 per cent H_2SO_4) the migration number changes so much with the amount of acid that calculating with the mean value is not permissible; in this case it would be necessary to integrate with reference to μ.[1] For the first three concentrations the value of ΔE is calculated by means of equation (25), because the measurements of Gladstone and Hibbert do not extend so far down:

TABLE IX.

Acid at the + Pb plate and $-PbO_2$ plate, % H_2SO_4	Acid at the $-$Pb plate and $+PbO_2$ plate, % H_2SO_4	p 18° C. mm. Hg.	u Mean.	$\Delta\epsilon_1$ Volts.		$\Delta\epsilon_2$ Volts.	
				Found.	Calc.	Found.	Calc.
0.2	0.65	15.3	0.800	0.036	0.023	0.054	0.034
0.2	1.35	15.3	0.800	0.047	0.041	0.072	0.061
0.2	2.85	15.3	0.810	0.060	0.060	0.095	0.090
0.2	5.5	15.1	0.813	0.066	0.068	0.107	0.111
0.2	10.5	14.9	0.821	0.082	0.082	0.134	0.128
0.2	14.5	14.5	0.823	0.094	0.091	0.150	0.142
0.2	18.0	14.0	0.823	0.102	0.100	0.158	0.156
0.2	22.5	13.2	0.818	0.109	0.112	0.168	0.175
0.2	36.5	10.0	0.805	0.150	0.14	0.215	0.25
0.2	48.0	6.2	0.778	0.164	0.18	0.281	0.34
0.2	57.5	—	—	0.204	—	0.359	—
0.2	85.5	—	—	0.247	—	0.573	—
0.2	98.0	—	—	0.266	—	0.643	—

[1] The integration of the equation for the dilution coefficient given below gives directly the equation to be employed for higher concentrations:

$$\Delta\epsilon_1 = -\frac{RT}{2}\int_{n_1}^{n_2} \mu n \frac{\partial \ln p}{\partial n} dn.$$

We will now turn our attention to the peroxide concentration chain:

$PbO_2 \mid PbSO_4$ conc. H_2SO_4—dilute $H_2SO_4 PbSO_4 \mid PbO_2$.

In this, as in the lead chain, the passing current liberates 1 mol. SO_4 in the dilute acid and binds one in the concentrated. In addition 2 O atoms are removed for the formation of peroxide from the dilute solution and added to the concentrated. In this chain, as distinguished from the other, 2μ H atoms wander from the dilute to the concentrated and $(1-\mu)$ SO_4 molecules in the opposite direction, for the current in the peroxide concentration chain flows in the opposite direction from that in the lead concentration chain. The total transportation per $2F$ is then

$$1SO_4 - 2O - 2\mu H + (1-\mu)SO_4 = (2-\mu)H_2SO_4 - 2H_2O.$$

Since the distillation work equivalent to the transportation of the water is $2RTln\frac{p_2}{p_1}$ (p_2 = vapor-pressure of the dilute acid, p_1 = vapor-pressure of the concentrated acid), we get for the E.M.F. of the peroxide concentration chain

$$\Delta\varepsilon_2 = 0.990 \times 10^{-4} T\left((2-\mu)f(p) + \log\frac{p_2}{p_1}\right), \quad (36)$$

and after substituting the value for $f(p)$ in the same manner as before ($T = 290$),

$$\Delta\varepsilon_2 = (2-\mu)\frac{\Delta E}{2} + 0.0287\mu \log\frac{p_2}{p_1}. \quad (37)$$

The comparison of this expression with the measurements of Gladstone and Hibbert is given in the last two columns of Table IX. This series of measurements gives the E.M.F. of the accumulator for 0.2 per cent acid as 1.708 volts, indicating that in all probability these values were determined at a somewhat lower temperature than the $\Delta\varepsilon_1$ values. That which was said on p. 84 respecting the dilute and concentrated solutions also applies here.

When we consider the uncertainty of the bases of the calculation, the agreement between the calculated and found values of $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ is very satisfactory.

Especially of practical significance to the lead accumulator are the values of the dilution coefficients of the electrode potentials. By a course of development the same as for the entire accumulator (p. 65), we obtain from the above $\Delta\varepsilon$ values the dilution coefficients of the separate electrodes:

$$\frac{\partial\varepsilon_1}{\partial n} = -\frac{RT}{2}\mu \cdot n\frac{\partial \log p}{\partial n}, \quad . \quad . \quad . \quad . \quad . \quad (38)$$

$$\frac{\partial\varepsilon_2}{\partial n} = -\frac{RT}{2}\left((2-\mu)n+2\right)\frac{\partial \log p}{\partial n}, \quad . \quad (39)$$

from which follows, by division,

$$\frac{\partial\varepsilon_2}{\partial n} = \left(1.47+\frac{2.47}{n}\right)\frac{\partial\varepsilon_1}{\partial n} \quad . \quad . \quad . \quad (40)$$

if we introduce for μ, from the figures of Hittorf, the mean value 0.808 for the range of concentra-

tion from 0.2 to 30 per cent H_2SO_4. From this it follows that for the mixture 5 mol. H_2O to 1 mol. H_2SO_4 ($n=5$) the potential of the peroxide electrode falls off about twice as fast with the dilution as does that of the lead electrode. In Table X are a number of $\frac{\partial \varepsilon_2}{\partial n}$ values from the above measurements, compared with the same values calculated by equation (40):

TABLE X.

Per Cent H_2SO_4.	n	$\frac{\partial \epsilon_1}{\partial n}$. Observed.	$\frac{\partial \epsilon_2}{\partial n}$. Calculated.	$\frac{\partial \epsilon_2}{\partial n}$. Observed.
10.5	46.4	0.00082	0.0012	0.0010
18.0	24.8	0.0011	0.0017	0.0016
36.5	9.47	0.0058	0.0100	0.0093

We can interdependently calculate, then, in a very simple manner, with a fair approximation, the dilution coefficient of the individual electrodes.

For very dilute solutions $\frac{2.47}{n}$ disappears and the ratio of the dilution coefficients is alone determined by the migration number, which latter, according to Hittorf's measurements, is 0.80 for the concentration range 0 to 2 per cent H_2SO_4. Therefore for dilute solutions $\frac{\partial \varepsilon_2}{\partial n} = 1.50 \frac{\partial \varepsilon_1}{\partial n}$, and herewith also $\Delta \varepsilon_2 = 1.50 \Delta \varepsilon_1$. In fact, dividing the $\Delta \varepsilon$ values

for dilute solutions of Table IX, we get the figures 1.50 and 1.53. This agreement is a splendid confirmation of the accuracy of Hittorf's migration numbers.

(*b*) *Relations for Dilute Solutions.*

As a matter of course the simpler equations for the change of electrode potentials in dilute solutions could be derived from the above thermodynamic equations, in the same way as was done on p. 65 for the E.M.F. We arrive at these relations, however, in a much easier way than was done by Mugdan (l. c.) with the aid of Nernst's osmotic theory of concentration chains. If, in order to bring out more clearly the connection with above calculations, we likewise introduce the migration number μ, $\left(\mu = \frac{u}{u+v}\right)$, in place of the ion velocities u and v used by Mugdan, we get the E.M.F. of the concentration chains in the following manner:

In the concentration chain

$$\mathrm{Pb} \mid \mathrm{PbSO_4}\ \text{conc. acid—dil. acid}\ \mathrm{PbSO_4} \mid \mathrm{Pb},$$

with a current of $2F$ flowing through it, the quantity of acid μ g.-mol. $H_2SO_4 = 3\mu$ g.-ion [1] is carried from the higher concentration (c_2) into the lower (c_1). Since the osmotic pressure is proportional to the ion concentration, the osmotic work con-

[1] For in dilute solution sulphuric acid is decomposed into 2 $\overset{+}{H}$ ions and 1 $\overset{--}{SO_4}$ ion.

sumed for current production is given by the expression $3\mu RT \log \frac{c_2}{c_1}$ (compare foot-note, p. 37), and therefore the E.M.F.

$$\Delta\varepsilon_1 = \tfrac{3}{2}\mu \cdot RT \log \frac{c_2}{c_1}$$

$$= 3 \cdot \mu\, 0.990 \times 10^{-4} T \log^{10} \frac{c_2}{c_1} \text{volts.} \quad (41)$$

In the peroxide concentration chain

$PbO_2 \mid PbSO_4$ conc. H_2SO_4—dil. H_2SO_4, $PbSO_4 \mid PbO_2$

the quantity of acid transported per $2F$ is $(2-\mu)$ g.-mol. $H_2SO_4 = 3(2-\mu)$ g.-ion from the concentrated into the dilute acid, which corresponds to the osmotic work $3(2-\mu)RT \log \frac{c_2}{c_1}$. In addition, however, 2 mol. H_2O are carried in the opposite direction, which transportation is equivalent to the work $2RTln\frac{p_2}{p_1}$. In dilute solutions we can as a first approximation introduce for $ln\frac{p_2}{p_1}$ the expression

$$\frac{3(c_2-c_1)}{N} \quad (N = 55.5, \text{ see p. 69}).$$

Then we obtain for the E.M.F.

$$\Delta\varepsilon_2 = 3 \times 0.990 \times 10^{-4} T \Big((2-\mu) \log^{10} \frac{c_2}{c_1} + 0.016(c_2 - c_1) \Big) \text{volts.} \quad (42)$$

The addition of equations (41) and (42) of course gives the change of the E.M.F. of the entire accumulator, i.e., equation (23).

Equations (41) and (42) have also been subjected, by Mugdan, to a thorough experimental test. The results of his measurements, referred to 17° C. ($T = 290$), are contained in Table XI.

In the calculations 0.85 the value for μ recently found experimentally by Stark for the concentrations 2 to 5 per cent was used. The incomplete dissociation of the sulphuric acid was taken into account, by introducing, instead of the factor 3, the value 2.22. The considerable deviation between calculated and found in the case of the last two values (enclosed in brackets) is due to the fact that the equations hold good only for dilute acids, and this condition is no longer fulfilled for these concentrations. For the more dilute solutions the agreement between calculated and found values is very good.

TABLE XI.

Concentration per Liter of Solution.	Electromotive Force in Volts at the Negative Plates.		Electromotive Force in Volts at the Positive Plates.	
	Found.	Calculated.	Found.	Calculated.
$\frac{3}{8}$ g.-mol. – $\frac{3}{32}$ g.-mol.	−0.0308	−0.0329	0.0444	0.0446
$\frac{3}{4}$ g.-mol. – $\frac{3}{32}$ g.-mol.	−0.0462	−0.0494	0.0664	0.0676
$\frac{3}{16}$ g.-mol. – $\frac{3}{32}$ g.-mol.	−0.016	−0.0165	0.023	0.0224
$\frac{3}{8}$ g.-mol. – $\frac{3}{16}$ g.-mol.	−0.015	−0.0165	0.0225	0.0225
$\frac{3}{4}$ g.-mol. – $\frac{3}{8}$ g.-mol.	−0.017	−0.0165	0.021	0.0227
$\frac{3}{2}$ g.-mol. – $\frac{3}{4}$ g.-mol.	−0.021	−0.0165	0.029	0.0231
3 g.-mol. – $\frac{3}{2}$ g.-mol.	−0.0315	−0.0165	0.052	0.0238

The behavior of the separate accumulator electrodes, for the entire possible range of concentration, therefore also conforms to the theory. Wherewith, as Mugdan pointed out, we have another proof that the chemical action in the accumulator is expressed by our fundamental equation (1), and that both electrodes of the accumulator are absolutely reversible. In Chapter IX we shall become acquainted with an important practical application of these relations just developed.

VI.

TEMPERATURE COEFFICIENT.

THE variation of the E.M.F. of the lead accumulator with the temperature was first investigated by G. Meyer [1] on a Planté element with the acid concentrations 12.3, 27.8, and 45 per cent H_2SO_4. According to these experiments the E.M.F. showed itself independent of the temperature.

Another very extended study of the same subject we owe to F. Streintz,[2] who demonstrated, through a large number of measurements carefully executed, that although the temperature coefficient is very small, yet it is perfectly determinable. For the measurements he used small cells, with electrodes cut out of Tudor plates, warmed in a water-bath. The E.M.F. was determined by means of a galvanometer for every five degrees and the temperature coefficient calculated. The same was always positive and within acid densities 1.144 to 1.173, represented by the parabolic equation

$$\frac{\partial E}{\partial T} = 357 \times 10^{-6} - 0.64(E - 1.998)^2.$$

[1] Wied. Ann. 33, p. 278. 1888.
[2] *Ibid.* 46, p. 449. 1892.

The coefficient reaches a maximum at 3.41×10^{-4} volts with an acid density of 1.160 (22 per cent H_2SO_4).

In Table XII the results of the measurements of Streintz are given. The first column contains the measured E.M.F. at 10° C., the second the observed temperature coefficients, and the third the values calculated according to the above empirical formula.

TABLE XII.

E Observed.	$10^6 \frac{\partial E}{\partial T}$ Observed.	$10^6 \frac{\partial E}{\partial T}$ Calculated
1.9223	140	—
1.9828	228	213
1.9860	274	265
1.9920	333	335
2.0031	335	341
2.0072	312	305
2.0084	285	293
2.0090	279	280
2.0105	255	265
2.0779	130	—
2.2070	73	—

At the same time the fact was brought out that between 10 and 70 degrees the temperature coefficient is independent of the temperature, i.e., the E.M.F. is a linear function of the temperature.

We shall now attempt to account theoretically for the variation of the temperature coefficient.

We saw in Chapter II that the second law of thermodynamics gives the equation expressing the relation between temperature coefficient, electromotive force, and heat of reaction,

$$E = \frac{Q}{23073} + T\frac{\partial E}{\partial T}.$$

From this we get for the temperature coefficient directly

$$\frac{\partial E}{\partial T} = \frac{E}{T} - \frac{Q}{23073\,T}. \quad . \quad . \quad . \quad (43)$$

The heat of reaction Q varies only with the different concentrations of acid in consequence of the different values for the heat of dilution of the sulphuric acid. The quantity Q is therefore composed of a constant portion, and the particular values of U and U' (see p. 58). Equation (43) then takes the form

$$\frac{\partial E}{\partial T} = \frac{E}{T} + \frac{U - U'}{23073\,T} - \text{const.} \quad . \quad . \quad (44)$$

By means of this equation we can calculate the relative values of the temperature coefficient for different acid concentrations; however, only with a rough approximation, because slight errors in the values of U exert a great influence. Equation (44), like equations (16) and (17), upon which it is based, holds only for concentrated acids.

For very small acid concentrations the heat of dilution of sulphuric acid becomes insignificant,[1] so that Q assumes a value independent of the concentration. Besides, for dilute acids the E.M.F. is determined by the acid concentration c (g.-mol. per liter) according to the equation (p. 66)

$$E = 1.92 + 0.15 \log^{10} c.$$

[1] Law of the thermoneutrality of dilute solutions.

From this we get by equation (43) the expression for the temperature coefficient at 18° C. ($T = 291$)

$$\frac{\partial E}{\partial T} = 0.52 \log^{10} c + \text{const. millivolts.} \quad . \quad (45)$$

This equation holds for the concentration range $c = 0.1$ to $c = 0.0005$. It shows that below the acid concentrations investigated by Streintz the temperature coefficient must very rapidly fall off to zero, and for small values of c will assume large negative figures. To test this conclusion of the theory, I have continued the investigations of Streintz and extended the measurements through the entire possible range of concentration. For this purpose a small cell, built of chemically pure substances, was filled with acids of varying concentration and the E.M.F. determined at 0° and 24° C. after the cell had been kept at the particular temperature for six hours and the potential remained unchanged. Following each measurement the accumulator acid was titrated to determine whether the concentration had been changed by spontaneous discharging. If this was the case (and with very dilute acids it was unavoidable), the measurement at 0° C. was corrected by the accurately known acid coefficient for this temperature.

The results are contained in Fig. 4.

Below $c = 2$ the temperature coefficient corresponding to the equation (45) rapidly diminishes. At an acid concentration of 0.70 g.-mol. H_2SO_4

per liter the E.M.F. becomes independent of the temperature, and with very dilute acids rapidly diminishes with rise in temperature. *The temperature coefficient has therefore positive as well as negative values, depending upon the acid concen-*

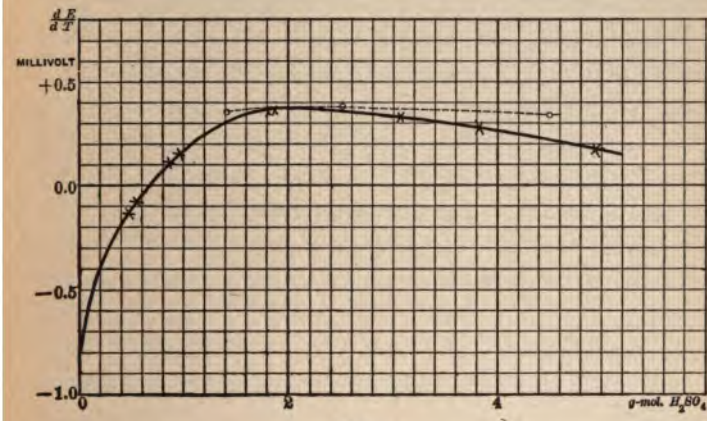

FIG. 4.

tration. The above measurements also show clearly the maximum of temperature influence found by Streintz. In part, however, the absolute values of the temperature coefficient are considerably larger than those found by Streintz (Table XII), which is explained by the fact that he made the measurements directly after the warming, while the above values were obtained after the cell had been kept for a long time at the particular temperature.

Calculating from the heat of dilution of sulphuric acid, by equation (44), the variation of the tempera-

ture coefficient for the more concentrated acids, we obtain the dotted curve. Here also the maximum of the temperature coefficient is very marked. With increasing concentration, however, the calculated values diminish considerably more slowly than the measured values. This is very probably caused by the rapid increase of the direct attack of the lead sponge by the acid with rise in temperature, and therefore the measured electromotive forces come out too small at a higher temperature. The measurements given in Fig. 4 also permit of several conclusions as to the thermic changes in the accumulator. While, on the one hand, a cell filled with the acid of the usual density (1.15) heats during charging and cools during discharging, corresponding to the positive temperature coefficient and as the calorimetric measurements of Streintz (Chap. II) have shown; on the other hand an accumulator with acid whose density lies below 1.044 works during charging with an absorption of heat and during discharging with a liberation of heat. In the case of a concentration of acid of 0.70 g.-mol. H_2SO_4 per liter heat is neither given up to nor taken from the surroundings.

If we determine the heat developed in a cell in action, the so-called secondary heat, the temperature coefficient can be calculated from the same. Unfortunately such measurements employing dilute acids have not been carried out as yet; for more concentrated solutions, however, we have several determinations of Streintz, which were

discussed in Chapter II. Calculating the temperature coefficient from the measured secondary heats, we obtain the values contained in Table XIII, which, considering the many errors to which such measurements are subject, amply confirm the above determinations of the temperature coefficient.

TABLE XIII.

Acid Density.	Second. Heat, Watt-sec.	$\frac{\partial E}{\partial T}$ (Millivolts).		
		Calculated.	Measured.	
			Streintz.	Author.
1.155	0.094	0.35	0.33	0.36
1.153	0.089	0.32	0.32	0.37
1.237	0.046	0.17	0.15	0.25

As stated, Streintz found that the E.M.F. is a linear function of the temperature. The same is still true in the case of highly dilute acids, as can be seen from Fig. 5, which represents the variation of the E.M.F. with the temperature at an acid concentration of about 0.0005 g.-mol. H_2SO_4 per liter. At the same time a glance at this figure shows that, using very dilute acid, one can make a very effective thermoelement out of the accumulator, by taking two batteries filled with such acid, connecting them opposed to each other and keeping one at a low temperature, say 10° C., the other at

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a higher, for example 100° C. We have then at our disposal a potential of 0.6 volt per cell. If the cold battery is discharged, the warm one is charged and all that is necessary in order to enable

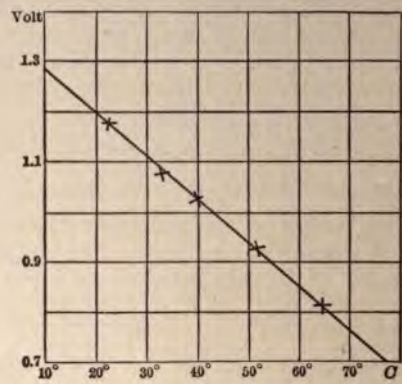

FIG. 5.

the system to give a current again at the expense of the introduced heat is to warm the former and cool the latter, and so on. It goes without saying that an accumulator filled with such dilute acid is not a technically available apparatus. It is, however, within the range of possibility that the high temperature coefficient may be obtained with a suitable and practical electrolyte. The lead-peroxide-lead element would then not only be an excellent accumulator, but at the same time a first-class current generator, making the steam-engine dispensable for producing electricity.

VII.

INFLUENCE OF EXTERNAL PRESSURE.

THE influence of external pressure upon the E.M.F. of the accumulator is only very slight, and therefore of no practical significance. Since, however, the effort has repeatedly been made to increase artificially the E.M.F. or capacity by applying high pressure, we will carry out the simple calculation which shows that these are along the wrong course.

In order to determine the change in the E.M.F. which can be brought about by an increase in the pressure resting upon the cell, let us picture to ourselves two accumulators connected with poles opposing each other (like poles connected). The two are to be identical as far as density of acid, temperature, etc., are concerned, except that resting on accumulator 1 we have the pressure p_1, and on accumulator 2 the greater pressure p_2. Now if the E.M.F. of accumulator 2 (E_2) is greater than that of accumulator 1 (E_1), we can get an electric current (energy) from the cells opposing each other, produced by the difference of electromotive forces ($E_2 - E_1$). If we allow 96540 coulombs to pass the circuit, corresponding to the reaction of

$\frac{1}{2}$ g.-mol. Pb and PbO_2, we obtain in the outer circuit an available work

$$W_1 = 96540(E_2 - E_1) \text{ volt-coulombs.}$$

Herewith accumulator 2 is discharged and accumulator 1 is charged with the same quantity of electricity; and in accumulator 2 the same chemical substances are decomposed and formed as are respectively formed and decomposed in accumulator 1. We can therefore easily bring the cells back to their original condition, in that we transfer, for example by isothermic distillation, osmosis, and the like, to accumulator 2 the $\frac{1}{2}$ g.-mol. Pb, $\frac{1}{2}$ g.-mol. PbO_2, and 1 g.-mol. H_2SO_4 formed in accumulator 1, and the 1 g.-mol. $PbSO_4$ and 1 g.-mol. H_2O formed in 2 to 1. This is possible without requiring the least amount of work, since the substances in both cells are to be present in the same concentration. Therefore during the production of current the work of the chemical action is zero, taken altogether, and the equivalent of the electrical energy gained is the work performed by the external pressure in the cells.

If we indicate the change in volume which takes place when $\frac{1}{2}$ g.-mol. of active mass in the accumulator changes, by Δv, then we gain the work $p_2 \Delta v$ in accumulator 2, while in accumulator 1 the work $p_1 \Delta v$ is consumed. Measuring v in liters, p in atmospheres, the work performed by the external pressure in the production of current is

$$W_2 = (p_2 - p_1)\Delta v \text{ liter-atmospheres.}$$

Now since one liter-atmosphere is equivalent to 101.3 volt-coulombs, it follows that

$$W_2 = 101.3(p_2 - p_1)\Delta v \text{ volt-coulombs,}$$

and the equation of the electrical and mechanical energy gives ($W_1 = W_2$)

$$E_2 - E_1 = 1.04 \times 10^{-3}(p_2 - p_1)\Delta v \text{ volts.} \quad . \quad (46)$$

In addition we still have to calculate the change in volume Δv. The densities and volumes of the substances concerned are given in Table XIV.

From these figures we get the volume of the actual substances before reaction (discharge) to be 58.37 c.c., and after reaction 66.7 c.c., i.e., the change in volume,

$$\Delta v = -8.3 \times 10^{-3} \text{ liters.}$$

During discharge an increase in the volume of the accumulator takes place, while during charging we have a decrease, the change per ampere-hour being 0.3 c.c.

TABLE XIV.

	Density.	Volume	
		of	cc.
Pb	11.38	½ g.-mol.	9.10
PbO_2	8.91	" "	13.41
$PbSO_4$	6.23	1 g.-mol.	48.7
H_2SO_4	2.73[1]	" "	35.86
H_2O	1.00	" "	18

[1] This value represents the apparent density of the sulphuric acid in a 20 per cent solution; it is so high because upon mixing sulphuric acid with water a very marked volume contraction takes place.

The specific gravities of the substances in the above table vary considerably, so that the calculation of Δv becomes somewhat inexact. I have therefore measured directly the change in volume during discharge for a 20 per cent acid, by enclosing a small accumulator in a glass vessel (Fig. 6) and reading the increase in volume on the graduated stem R which was produced by a discharging current of 1 ampere-hour. During the experiment the apparatus was kept in a water-bath of constant temperature.

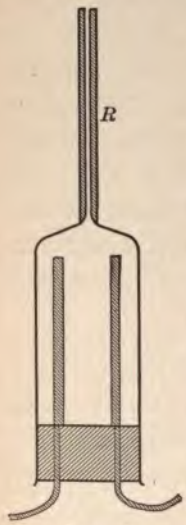

FIG. 6.

The result was an increase in volume of 0.42 c.c. for each ampere-hour of discharge. The more accurate value for Δv is, therefore,

$$\Delta v = -11 \times 10^{-3} \text{ liters.}$$

Introducing this value into above equation, we get

$$E_2 - E_1 = -11.4 \times 10^{-6}(p_2 - p_1) \text{ volts.} \quad . \quad (47)$$

That is, an increase in the external pressure does not bring about an increase but a decrease in the E.M.F., amounting to 0.0011 volt per 100 atmospheres. The effect of pressure upon the E.M.F. of various galvanic elements has been measured by Gilbault.[1] For the accumulator, using 8.8 per

[1] Compt. rend. 113, p. 465. 1891.

cent acid, he found a decrease in the E.M.F. of 0.0012 volt per 100 atmospheres rise in pressure, a good agreement with the above calculation.

While pressure has a detrimental effect upon the E.M.F. it acts favorably upon the capacity of the cell, by retarding somewhat the developing of gas during charging, and therefore the cell takes up a greater quantity of current.

In the bubbling accumulator, however, the gases are, as it is, liberated under very high pressure, so that the influence of pressure on the capacity of the cell is likewise very slight and without any practical significance.

VIII.

BEHAVIOR DURING CHARGING AND DISCHARGING.

In the previous chapters we have treated the variation of the E.M.F. produced by various external influences. All these considerations pertained to the accumulator while no current was flowing; there are still to be discussed the variations of the electrical magnitudes which take place in the cell while the current is flowing.

The work that may be performed by an accumulator in the external circuit is essentially determined by the capacity and the potential at the poles, the so-called pole-potential of the closed cell.

The pole-potential, as is well known, is given by Ohm's law during charging

$$K = E + I \cdot R, \quad . \quad . \quad . \quad . \quad . \quad (48)$$

during discharging

$$K' = E - I \cdot R, \quad . \quad . \quad . \quad . \quad . \quad (49)$$

where E stands for the E.M.F. of the cell, R the internal resistence, and I the strength of current.

Keeping the current at a constant strength and measuring the pole-potential at short intervals, we obtain curves of the form given in Fig. 7. During the first minutes of charging the E.M.F. rapidly rises from 2.0 to about 2.1 volts, then during the greatest part of the charging it slowly, steadily rises, finally at the close suddenly going up to 2.5–2.7 volts. During the time of the rapid rise in the potential, the cell begins to evolve gas, and the pole-potential changes only very slightly. If we now interrupt the current and allow the charged accumulator to rest, the potential at first falls rapidly, later slowly, reaching, in the course of several hours, the E.M.F. corresponding to the density of the acid employed. Further discharging shows another rapid fall in potential to about 1.9 volts; from here on it gradually sinks to about 1.85 volts, finally decreasing more and more rapidly to zero. The values given in Fig. 7 pertain to about 20 per cent acid and a normal current density of about 0.005 ampere per sq. cm. of electrode area. In the case of higher current densities the distance between the charging and discharging curve increases and the straight portions of the curves form a greater angle with the axis of abscissa.

With elements having a thin active layer (Planté cells and the like) the bends of the curves become more marked, with those having thick plates they are more rounded than in Fig. 7. The general character of the curves, however, remains unchanged.

Fig. 7 shows that the pole potential is several tenth volts higher during charging than during discharging, whereby the 20 to 30 per cent loss of energy always accompanying the storage in the accumulator is brought about. It would seem

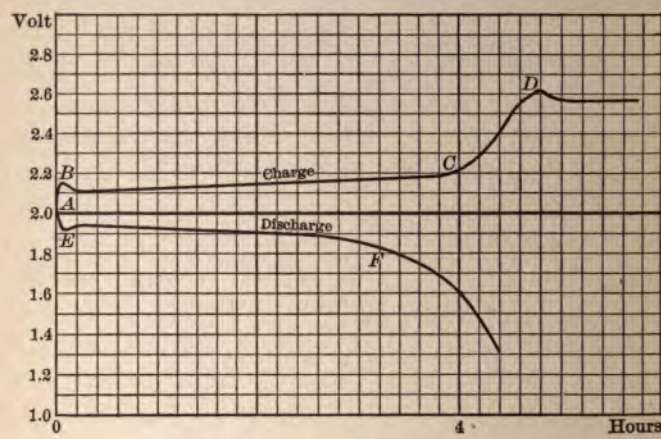

FIG. 7.

near at hand to ascribe this difference in the values of K to the loss of potential (IR) in the cell. The internal resistance, however, of even the smallest cells employed, in open circuit is not more than several hundredth ohms. In order to explain this large loss in potential we would have to assume, during the flowing of current, an increase of the resistance from 20 to 40 times the amount. Such changes in resistance could easily be observed with telephone and alternating current. The measure-

ments of Haeberlein,[1] who was the first to study these relations more in detail, showed, however, that such an increase in the resistance does not take place. Therefore the difference between the charging and discharging potential can only be brought about by a change in the E.M.F. (E), i.e., by a polarization of the electrodes. Very different views have been expressed as to the cause of this polarization; Haeberlein assumed a gas polarization, other investigators (Gladstone, Hibbert, Schoop) suspected an insufficient amount of active mass or acid; newer theories (Darrieus, Elbs) attempted to explain the same by assuming for charging and discharging different chemical reactions taking place with unequal change in the amount of energy. The assumption of a gas polarization seems untenable, because at a voltage of 2 no gases are liberated in the accumulator, similarly an insufficiency of active mass is excluded since the falling off of the voltage takes place at the very beginning of the discharging when active mass is present in large excess. The assumption of a charging reaction with a greater change in energy will be disproven in the following chapter; wherewith the only cause remaining for the difference between the charging and discharging voltage is the appearance of variations in the concentration of the acid, and partly also the dissolved salts, within the substance of the plates. In fact, as will be shown presently, the entire behavior of the

[1] Wied. Ann. 31, p. 393. 1887.

accumulator during charging and discharging finds its best explanation in this last assumption.

That decided changes in the concentration of the acid will set in at the electrodes is very probable when we remember that the active substance at both poles is a porous, spongy mass; consequently the sulphuric acid set free during charging according to equation (1) can only slowly diffuse out and the concentration of the acid in the substance of the electrode must rise. As is well known during the charging of an accumulator one observes convection currents of more dense acid flowing down the electrode plates. Conversely during discharging the concentration of the acid within the mass of the electrode will diminish. Now, through the measurements and calculations in Chapter IV it was proven that the E.M.F. rises greatly with the acid concentration; it is apparent, then, why the charging potential lies several tenth volts higher than the discharging potential. What is more, to explain this difference it is by no means necessary to assume any very great variations in concentration. With the usual current densities the mean E.M.F. during charging lies about 0.08 volt higher, during discharging about as much lower, than corresponds to the density of the acid present; according to Table V, therefore, the concentration of the acid in the electrode substance is about 10 per cent H_2SO_4 higher during charging, and about the same amount lower during discharging, than the acid outside. That is with normal charg-

ing the concentration of the acid within the active mass rises from 20 to 30 per cent and falls during discharging down to 10 per cent. Of course, with greater current densities the concentrating and diluting of the electrode acid assumes greater values, resulting in a greater diminution of the discharging and a larger increase in the charging potential.

The fact that the polarization appearing in the working accumulator is caused principally by variations in the concentration of the acid and only to a limited extent by the shortage or excess of

$$\underset{PbO_2}{--} \quad \underset{Pb}{++}$$

the other ions (PbO_2, Pb) can be shown by measuring the pole-potential with different acid densities. With more dilute acid, of course, the reduction in concentration will be more intensified for the same strength of discharging current resulting in a greater polarization of the accumulator.

A small cell discharged with the high current density of 0.01 ampere per sq. cm. gave, for example, with an acid density of 1.18 (25 per cent H_2SO_4) the E.M.F. of 2.02 volts in open circuit and a mean discharging potential of 1.80 volts; the polarization therefore amounted to about 0.22 volt. On the other hand, with an acid density of 1.06 (9 per cent H_2SO_4) the E.M.F. was 1.94 volts, the mean discharging potential 1.66 volts, and consequently the polarization 0.28 volt.

The marked variations in concentration occurring at the electrodes can readily be demonstrated by

a simple lecture experiment. Take two electrode strips cut from larger plates and suspend them three-quarters of their height in a flat trough [1] of plain parallel glass plates about $2 \times 4 \times 6.5$ cm. in dimensions. Project an enlarged picture of this small cell by means of a projecting apparatus, then by charging with about 0.3 ampere one can see flowing down the electrodes, and especially beneath the same, decided convection currents of concentrated acid. During discharging the reverse takes place, convection currents of dilute acid rise along the electrodes. Also the fact, to be discussed presently, that the variations in concentration are greater at the positive than at the negative plate is clearly visible. We will now consider more in detail the course of the pole-potential curves, taking up first the charging curve (Fig. 7).

(*a*) *Charging Curve.*—Upon closing the charging current through an accumulator, sulphuric acid is at once set free at both electrodes from the lead sulphate, the E.M.F. and charging potential therefore rise rapidly (portion *AB* of curve) until the difference in concentration against the external acid has become so great that the acid equalization can hold pace with the fresh formation of the same.

Shortly after the first rising of the potential the same usually falls again a bit. This peculiar phenomenon is in all probability to be attributed to the destruction, by the action of the charging

[1] To be had of Leybold's successor, Cologne.

current, of the thin continuous layer of sulphate which forms on the electrodes during rest. This results in a diminution of the internal resistance, and therefore, according to equation (48), in a decrease of K. In the case of highly sulphated electrodes, this first potential maximum can amount to a number of tenth volts.

The slow linear rise during the greater part of the charging (portion BC of curve) is to be ascribed, on the one hand, to the increase in the density of the entire acid, and, on the other hand, to the deeper penetration of the current lines into the active mass and the accompanying greater difficulty of acid equalization.

Toward the end of the charging the voltage begins suddenly to rise very rapidly to 2.5–2.7 volts (portion CD of curve), and at the same time a strong evolution of gas sets in at the electrodes. This great rise in the voltage of 0.5 volt can, of course, not be caused by a concentrating of the acid, because at this stage of the charging practically all the sulphate accessible to the action of the current has been transformed, and the formation of acid has been replaced by a water decomposition.

This excess voltage of 0.5 volt may possibly come about as follows:[1] During charging there is always solid, finely divided lead sulphate present at the electrodes; the acid will therefore be kept very

[1] Nernst and Dolezalek, Zeitschr. f. Elektrochem. 1900.

nearly saturated with sulphate. At the close of the charging, however, almost all the sulphate accessible to the action of the current is consumed, and consequently the sulphate found in solution will be rapidly electrolyzed out, whereby the concentration of the lead ions diminishes and the E.M.F. must greatly increase according to equation (13) (p. 50). Very soon the lead solution is so greatly diluted that the work required to separate lead (ε_p) has become equal to that, which is necessary for the formation of hydrogen bubbles on a lead surface. From this moment on not lead but hydrogen will be separated. Analogous considerations can be developed with regard to the peroxide electrode.

That in reality a diminution of the lead sulphate concentration can produce an increase in the E.M.F. of a number of tenth volts is shown by measurements of Streintz,[1] according to which the potential difference of an oxidized (and therefore covered with sulphate) lead plate in sulphuric acid against zinc amounts to 0.45 volt, while a bright lead plate shows 0.75–0.77 volt. That is, the potential difference of a plate practically free from sulphate is about 0.3 volt higher against PbO_2 than one covered with sulphate.

If the overcharged accumulator is allowed to rest with open circuit, lead sulphate, which is still present, even in the charged element, will diffuse

[1] Wied. Ann. 41, p. 97. 1890.

out from the interior of the plate and thereby bring about the rapid fall of the E.M.F. to the normal amount. If all the sulphate found upon the electrode has been decomposed by a long overcharging, it is reformed of its own accord by spontaneous discharging when the circuit is opened. This is shown by the brief, energetic evolution of hydrogen upon interrupting the charging current. It seems safe then to assume that the high potential at the close of the charging is caused by the formation in the accumulator of a lead sulphate concentration chain.

Soon after the swelling of the potential up to the maximum value of 2.5 to 2.7 volts (according to the current density) it falls a number of hundredths volt (at *D* in Fig. 7); this comes from the fact that now the evolution of gas mixes the concentrated acid still present in the electrodes with the external acid. This mixing of the acid by the gas-bubbles can be directly observed very nicely in the lecture experiment described above.

(*b*) *Discharging Curve* (see Fig. 7).—According to our reaction-equation (1), the acid is used during discharging for the formation of sulphate; in immediate proximity to the electrode the concentration of the acid must diminish and therefore also the pole potential decrease (portion *AE* of curve). Soon after this follows a (however not always present) flattened potential minimum (at *E*), which is possibly caused by the formation of a supersaturated lead sulphate solution; for

the solubility of lead sulphate in 20 per cent acid perceptibly diminishes with dilution, so that at the beginning of the discharging when little solid lead sulphate is present a supersaturation of short duration is quite probable, but an increase in the lead sulphate concentration is accompanied by a diminution of the E.M.F. (equation (13), p. 50).

The further gradual falling off of the pole voltage (portion *EF* of curve) in the course of the discharge is caused by the decrease of the acid density in the entire accumulator, but above all by the increasing difficulty of the transportation of acid, as the action of the current penetrates deeper into the active mass. Finally, the rate at which the acid penetrates fails to keep pace with the electrolysis, which brings about the more and more rapid sinking of the pole-potential. This marked falling off naturally takes place earlier the greater the acid consumption, the stronger the current with which the accumulator is discharged. There can be no thought of a shortage of active material at the falling off of the discharge voltage, because it is still possible for some time to take energy from the accumulator by means of a weaker current.

The advance of the chemical change of the active mass of the positive electrode during charging and discharging has been analytically followed up by Ayrton, Lamb, and Smith. The results of these investigations are given in Fig. 1 (p. 7). The same show that during charging the entire sulphate is oxidized to peroxide (and probably

also reduced to lead sponge), while during discharging, even in the outer layers during the long discharging time of fifteen hours, only about 60 per cent of the active mass takes part in the current production; not until we use very weak currents is the electrode mass entirely converted into sulphate.

Gladstone and Tribe made a very interesting observation while discharging Planté cells with a strong current. After such a rapid discharge the negative electrode was covered with a dark coating. The analysis of this showed that the lead sponge is not only converted into sulphate but part of it even into peroxide.

They have given no explanation for this phenomenon, which is in the highest degree an unexpected one. The energy set free at the positive electrode in the conversion of peroxide into sulphate cannot possibly, in view of the loss of potential, suffice to convert sulphate back into peroxide at the other electrode.

But even this observation of Gladstone and Tribe is explained very simply by the variations in concentration occurring at the electrodes.

In the case of Planté cells the capacity of the peroxide electrode is usually considerably greater than that of the lead sponge electrode, so that during discharge the decrease in the concentration of the acid can be much greater at the latter than at the former. At the end of the charging, therefore, we have in the cell a peroxide concentration

chain of the kind discussed on p. 86, in which in the concentrated solution the peroxide is converted into sulphate, while in the dilute solution the sulphate is converted into peroxide with a force equal to a number of tenth volts (Table IX). For analogous reasons it is very probable that one can observe a partial reduction of the peroxide to lead sponge by rapidly discharging a Planté cell whose positive electrode has a lesser while its negative has a greater capacity.

IX.

REVERSIBILITY.

THE behavior during charging and discharging, described in the previous chapter, shows clearly that the loss of energy which takes place in the working accumulator, evidenced through the difference between the charging and discharging potential, is conditioned upon the development of variations in the concentration of the electrolyte within the active mass. It still remains to be proved that this applies to the entire energy loss and that it is not caused in part by a charging action of a higher decomposition voltage, as has been assumed in some of the newer theories. This question can easily be decided by rapidly passing from charging to discharging and plotting the voltage curve. In the second case the voltage would have to change abruptly with the change in current; in the first case, however, it would require a certain time and quantity of current, since the difference of concentration already present must first equalize itself and then develop in the opposite sense. An experiment in this connection upon a small accumulator is given in Fig. 8.

The charging and discharging took place with the accumulator in a state of semi-discharge, and was carried out with constant (normal) strength of current. The time is plotted as abscissa and the voltage as ordinate, after correcting for the

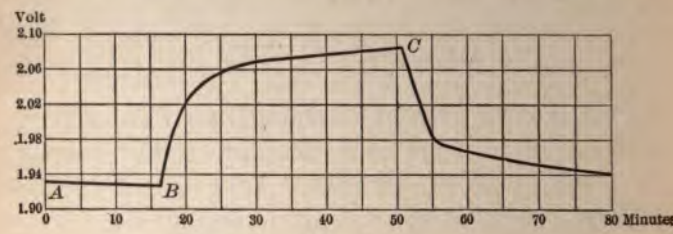

FIG. 8.

loss of potential of 0.05 volt corresponding to a resistance of 0.025 ohm, caused by the internal resistance.[1]

AB represents the middle section of a normal discharge curve. At *B* the direction of the current in the accumulator was suddenly changed by means of a commutator. As Fig. 8 shows, the counter potential of the accumulator did not rise abruptly, but gradually, to the charging voltage after about 10 amp.-min. had passed. At *C* the commutator was again changed to discharge, whereby the voltage gradually, after a passage of about the same amount of electricity as above, fell to the

[1] According to the measurements of Haagn (Zeitschr. f. Elektrochem. 1897) the resistance of a very similar accumulator employing the same acid is 0.013 ohm; therefore this proof is to be considered exact for only $\frac{9}{10}$ of the entire difference of potential.

smaller discharge voltage. In addition to these curves, the well-known fact that the difference between charging and discharging voltage increases with increasing strength of current and converges toward zero with decreasing strength speaks for the assumption of a concentration force and against a changed electrolytic reaction. Fig. 9 gives measurements which confirm this splendidly,

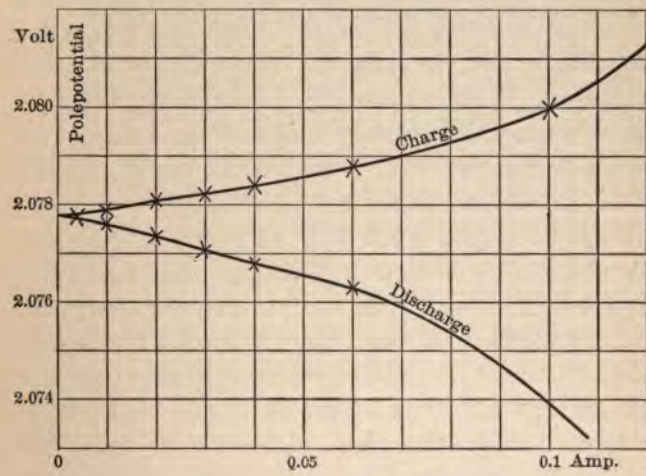

FIG. 9.

the charging or discharging strength of current being plotted as abscissa and the charging or discharging voltage as ordinate. The measurements were carried out on a large accumulator of the Watt Accumulator Works (Berlin), of about 200 amp.-hours capacity, having 6 positive and 7 negative plates, 28 × 17 cm. and 4 mm. thick, placed

formation of sulphate; in addition 2μ H atoms wander away and $(1-\mu)$ mol. SO_4 come, indicating the Hittorf migration number of the cathion $(\overset{+}{H})$ by μ. The total change in concentration at the lead-sponge electrode is therefore

$$-1SO_4 - 2\mu H + (1-\mu)SO_4 = -\mu \text{ mol. } H_2SO_4.$$

At the peroxide electrode we have the following changes in concentration: 1 mol. SO_4 is likewise used for the formation of the sulphate, at the same time 2 O atoms of the peroxide are sent into the solution. Through migration 2μ H atoms come and $(1-\mu)$ mol. SO_4 wander away. The total change therefore is

$$-1SO_4 + 2O + 2\mu H - (1-\mu)SO_4 = 2H_2O - (2-\mu) \text{ mol. } H_2SO_4.$$

The migration number μ of sulphuric acid is, according to the measurements of Hittorf, for the customary acid concentration of 20 per cent, equal to 0.81. Hence for this density of acid the consumption of acid at the lead-sponge electrode amounts to -0.81 mol. H_2SO_4, and at the peroxide electrode to 2 mol. $H_2O - 1.19$ mol. H_2SO_4, which latter change in water and acid means a change of -1.28 mol. H_2SO_4 for acid alone. Even though migration strives to reduce the concentration at the lead-sponge electrode and increase it at the peroxide electrode, nevertheless the reduction in concentration at the latter is considerably (about

1.6 times) greater, as a result of the formation of water. In addition, as already mentioned, the less great porosity of the peroxide also brings about a greater exhaustion of the acid at this electrode.

Now in Chapter V (p. 87) we obtained for the variations of the separate electrode potentials (ε_2 and ε_1) resulting from the dilution of the acid the equation

$$\frac{\partial \varepsilon_2}{\partial n} = \left(1.47 + \frac{2.47}{n}\right)\frac{\partial \varepsilon_1}{\partial n},$$

in which n stands for the number of g.-mol. of water which are contained in the acid solution per g.-mol. H_2SO_4. For the usual acid density of 1.15, $n = 20$, and therefore

$$\frac{\partial \varepsilon_2}{\partial n} = 1.6\frac{\partial \varepsilon_1}{\partial n};$$

that means that the potential of the peroxide electrode falls off with the dilution of the acid 1.6 times more than that of the lead electrode.

So the same change in concentration effects a 1.6 times greater polarization at the peroxide electrode than at the lead electrode. From all this it follows that the reversibility of the peroxide electrode will be considerably less than that of the lead electrode. Measurements on the reversibility of the single electrodes were first carried out by Streintz. The potentials of the separate electrodes of a Tudor cell of about 50 amp.-hours capac-

ity were measured against a zinc electrode in like acid, during charging and discharging with 6 amp.; in this way the values given in Fig. 10 were obtained.

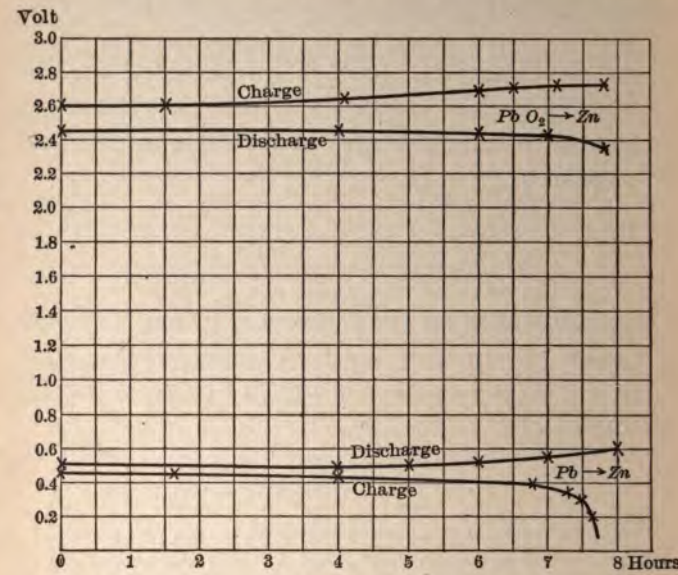

FIG. 10.

These values show that in reality the difference between the charging and discharging potential is considerably greater with the peroxide than with the lead electrode. Accurate quantitative relations are not to be expected with such complicated diffusion processes.

Mugdan[1] recently also investigated the polarization of the separate electrodes during charging

[1] l. c. p. 320.

and discharging. A positive and a negative grid plate, both made up of like dimensions filled with the same quantity of lead, were charged and discharged between larger plates. While the current was flowing, the positive plate was measured against a small peroxide plate and the negative electrode against a small lead-sponge plate. Here also, as shown in Fig. 11, the polarization of the positive

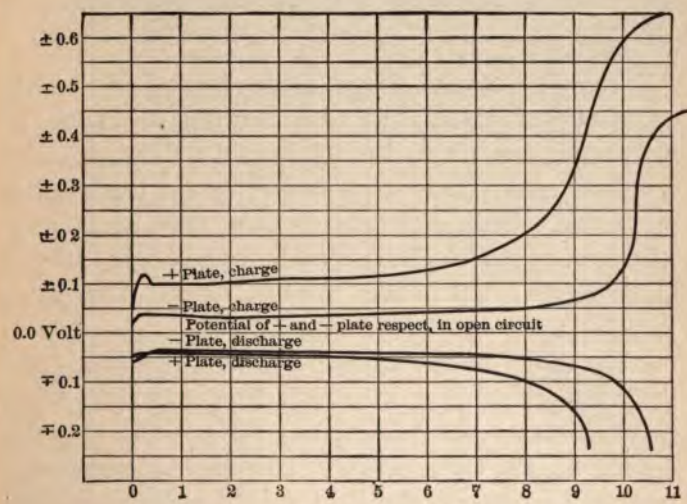

FIG. 11.

electrode is much greater than that of the negative. It is very remarkable, however, that the difference between the polarizations is considerably greater for charging than for discharging. Possibly this phenomenon is caused by the not rapid enough re-formation at the positive electrode, on account

of the exceedingly small concentration (compare p. 47) of the PbO_2 ions (p. 43) precipitated during charging; so that a perceptible exhaustion of these ions sets in, and according to the theory of Liebenow (equation 13) the charging voltage must rise. A decision upon this theoretically as well as practically important question might possibly be achieved by measuring the polarization of the peroxide electrode in solutions with varying concentrations of $\overline{\overline{PbO_2}}$ ions.

According to the above measurements of the loss of energy occurring in the accumulator, from 60 to 70 per cent is to be attributed to the peroxide and only from 30 to 40 per cent to the lead-sponge electrode. This of course is only true when positive and negative electrode are made of like frames and paste, and have approximately the same capacity.

In cells which contain thin positive and thick negative plates, or in which the capacity of the positive exceeds several times that of the negative electrode, the concentration polarization can nevertheless become greater at the lead sponge, in spite of the more favorable conditions described above, than at the peroxide. For the forms used in practice, however, the above relations may apply approximately.

X.

CHANGES IN THE OPEN CELL.

(*a*) *Recovery.*—If we discharge a cell until the pole-potential has fallen off and break the circuit, we observe on an attached voltmeter that the E.M.F. at first rises rapidly, later more slowly, and in the course of a few minutes reaches the value corresponding to the density of the acid present. This phenomenon has been termed "recovery of the accumulator." It fully resembles the residual charge observed upon rapidly discharging a condenser.

According to the statements of the previous chapter, the falling off of the E.M.F. comes from the acid poverty of the electrolyte within the active mass; after interrupting the current acid soon diffuses in from without and effects the recovery. That we have here essentially to deal with an action of diffusion is proven by the fact that the course of the recovery can with good approximation be calculated from the diffusion law of Fick.[1] The increase in concentration *dc*

[1] As is known, it applies only approximately in the case of electrolytes.

which the acid experiences in the small time interval dt can be placed approximately proportional to the difference between the concentration of the acid without (c_a) and within the pores (c_i), as well as the diameter of the pore q, and inversely proportional to the length of the pore l. We have, then,

$$dc = \text{const.} \frac{(c_a - c_i)}{l} q dt.$$

Since the concentration c_a of the outer acid can be considered constant and also q and l are independent of the time, we have

$$\frac{\partial c_i}{\partial t} = \text{const.} - \text{const.}\, c_i. \quad . \quad . \quad . \quad (50)$$

Now within the range of acid concentration of from 5 to 50 per cent the E.M.F. rises almost linear with the amount of acid, and hence, according to equation (15) (p. 53),

$$E = 1.850 + 0.00057\, c_i.$$

From this follows

$$\frac{\partial E}{\partial t} = 0.00057 \frac{\partial c_i}{\partial t},$$

and in conjunction with equation (50) and (15) we get

$$\frac{\partial E}{\text{const.} - E} = \text{const.}\, \partial t.$$

Finally, the integration of this equation gives for the E.M.F. at the time t the relation

$$E_t = E_a - \frac{p}{e^{at}}, \quad . \quad . \quad . \quad . \quad . \quad (51)$$

in which E_a, p, and a are constants, and e is the basis of natural logarithms.

For $t=\infty$, $E_t=E_a$; E_a then is the E.M.F. after complete recovery, as given by the concentration of the external acid.

For $t=0$, $E_t-E_a=-p$; p is the value of the polarization at the end of the discharge. Equation (51) makes it possible to calculate the E.M.F. at any time after closing the circuit from the E.M.F. at the moment of interrupting the discharge, the acid density, and a constant depending on the construction of the cell.

The rate of recovery has been carefully studied by Moore.[1] Out of the large number of measurements I give an example in Fig. 12. The drawn-out curve shows the course of the pole voltage during discharge. After breaking the circuit the voltage gradually rises again to the original value 2.052 volts, as indicated by the dotted curve. Calculating the electromotive forces at different times by means of equation (51), we get the values indicated in Fig. 12 by crosses which fit very well into the measured curve. In the calculation the values $E_a=2.052$, $p=E_a-E_{t_0}=0.264$, and $a=0.883$ were used.

[1] Physical Review, 4, p. 353. 1897.

This close agreement between the measured and calculated forces is again a splendid proof that the falling off of the pole voltage during dis-

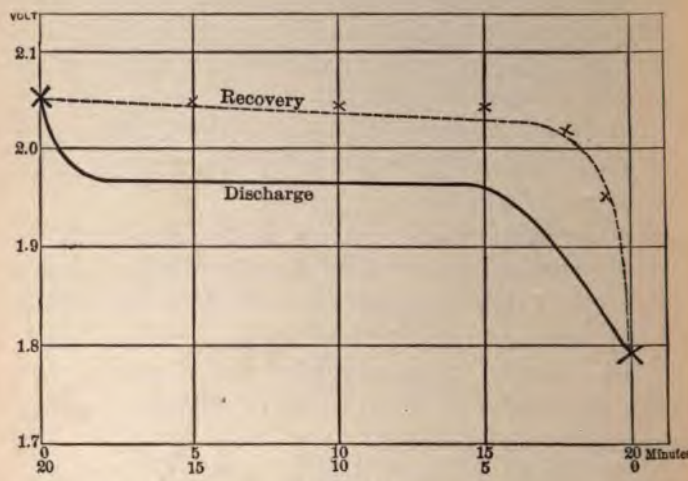

FIG. 12.

charge is essentially brought about by variations in concentration within the active mass, and not by an irreversible chemical action.

Quite similarly, as from an exhaustion through far-reaching discharge, the accumulator also recovers from a polarization through overcharging. As can be seen from Fig. 13, this recovery likewise shows a logarithmic course; here, however, it is not a diffusion of sulphuric acid, but one of lead sulphate (compare p. 114). The above considerations and equations are applicable to this case without further modification.

(*b*) *Self-discharge.*—If we allow a charged accumulator to remain idle, we observe that the density of the acid slowly decreases and that the amount of current obtainable by discharging becomes less from day to day. This spontaneous discharge

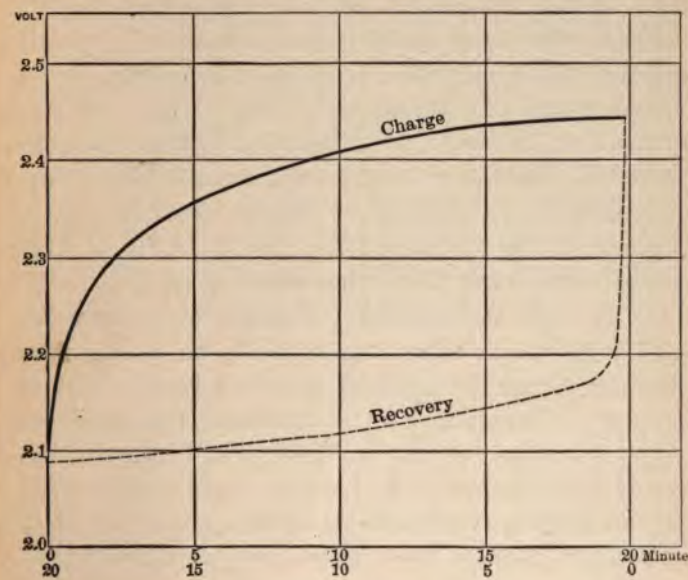

FIG. 13.

for a cell in good condition amounts to from 1 to 2 per cent per day of the stored quantity of electricity, and can, if the acid contains impurities, reach 50 per cent and more. We will first consider more in detail the causes for the self-discharge of the lead-sponge electrode, because practically this one is of the greater importance.

It is most fatal for the lead-sponge electrode to have the accumulator acid contaminated with a strongly negative metal, such as platinum, gold, and the like, since these precipitate on the lead and form with it a short-circuited local element, which causes the lead sponge to change into lead sulphate with a stronge evolution of hydrogen. Evidently such a self-discharge can be brought about only by a metal more electronegative than lead. In this connection, however, we must bear in mind that the potential difference of a metal against its solution, according to the theory of Nernst, does not alone depend on the nature of the metal, but in a high degree also upon the concentration of the metal ons in the surrounding electrolyte. Therefore lead behaves in accumulator acid, on account of the small concentration of the lead ions, about as strongly electropositive as cadmium in cadmium sulphate solution. It can then, for example, also precipitate nickel, cobalt, and even iron in sulphuric acid, but is incapable of doing so in solutions of easily soluble lead salts—a condition that is usually overlooked.

Further, it is to be noted that the local current formed, and therewith also the self-discharging, can only attain a value of practical significance when the liberation of hydrogen on the precipitated metal takes place readily. Now the quite recent investigations of Nernst and Caspari [1] have

[1] Zeitschr. f. physikal Chem. XXX, 1899, H. 1, p. 89.

shown that the electrolytic liberation of hydrogen on the surface of a metal does not by any means take place reversibly,[1] but in order to have hydrogen bubbles formed a considerable excess voltage is necessary, which has entirely different values for the different metals. According to these investigations the following voltages measured against a hydrogen electrode[2] are necessary for the production of hydrogen bubbles on the different metals:

Pt platinized	0.005 volt	Pd	0.46 volt
Au	0.02 "	Cd	0.48 "
Fe	0.08 "	Sn	0.53 "
Pt polished	0.09 "	Pb	0.64 "
Ag	0.15 "	Zn	0.70 "
Ni	0.21 "	Hg	0.78 "
Cu	0.23 "		

According to the measurements given in Table VIII (p. 79), the potential difference of a lead-sponge plate against a hydrogen electrode in sulphuric acid of the usual concentration is 0.33 volt. Therefore all metals having an evolution voltage for hydrogen smaller than 0.33 volt can cause a self-discharge of the lead electrode; all others, however, cannot. Consequently only the metals standing on the left in the above table are dangerous to the accumulator, while those on the right can be introduced into the acid without the least danger, even though some, such as tin,

[1] That is, at the potential zero measured against a hydrogen electrode.

[2] Platinized platinum-foil saturated with hydrogen.

mercury, and palladium, are considerably more noble than lead. On the contrary, a little mercury can even act to advantage, in that it alloys with the lead, thereby increasing the hydrogen evolution voltage of the same, which reduces considerably its spontaneous solution.

The intensity of the local current produced, i.e., the rate of spontaneous discharge, is of course, according to the above potentials, greatest for platinum and smallest for copper, as practical experience has long ago shown.

A detailed investigation as to the spontaneous discharge of accumulators by metallic impurities has been carried out by Kugel.[1] Spectroanalytical and chemical researches by Kayser and Ost, carried on at this opportunity, showed that platinum as an impurity even in the proportion of 1 : 1000000 is capable of producing a rapid self-discharge of the negative plate. Also the observation of Kugel s very striking, that metals can produce a strong self-discharge, which alone cause scarcely any action, when several are present in the acid at the same time. An explanation for this cannot be given at the time.

The spontaneous discharge produced by platinum is of especial significance practically, because this can easily occur when sulphuric acid is employed which has been concentrated in platinum retorts.

One can easily satisfy himself of the deleterious action of platinum by pouring a little platinum

[1] Elektrotechn. Zeitschr. 13, pp. 9 and 16. 1892.

chloride solution into a charged cell; in a short time the negative plates begin to give off hydrogen gas, and are soon completely discharged.

Such plates contaminated with platinum are in no wise to be made available again. All other metallic contaminations, in case they are present only in traces, become inactive upon continued used of the cell, supposedly, by gradually alloying with the lead.

The presence of metallic impurities may be recognized by the continued evolution of gas, at the negative plates, after interrupting the charging current.

We will now turn our attention toward the spontaneous discharge of the positive electrode. This in general takes place more slowly than that of the lead-sponge electrode, and therefore is of less importance in practice. Metallic impurities are of course without influence upon the lead peroxide, since they are not precipitated by it. The only kind of spontaneous discharge of interest here is the one investigated by Gladstone and Tribe and termed "local action." This action is based on the fact that the peroxide forms a short-circuited cell with the underlying body of lead, whereby peroxide as well as lead body are converted into sulphate. This attack of the peroxide upon the underlying lead accounts for the gradual destruction of the latter. The self-discharge coming about in this way reaches an extent which is of practical

significance only in cells with a thin peroxide layer (especially Planté cells).

In addition to the modes already discussed, the spontaneous discharge of a cell can be brought about by impurities which are easily oxidized and can serve as oxygen-carriers from anode to cathode. Such are in particular the salts of metals which occur in several states of oxidation. If, for example, a salt of iron is present, the same will be oxidized to ferric at the peroxide electrode, then diffuse to the lead-sponge electrode, and there pass into ferrous salt with the liberation of oxygen. This ferrous salt can then take up fresh oxygen again at the anode, and so on.

Another instance of this kind, investigated by v. Knorre,[1] is the self-discharge which manganese salts induce in the accumulator. Manganese compounds are often present as impurities in the litharge, or are possibly purposely added to the paste. Their deleterious action rests on the fact that permanganic acid is formed at the peroxide electrode, which diffuses to the lead sponge and there gives up the available oxygen. The use of manganese salts is therefore to be avoided, especially as there seems to be no favorable influence upon the active mass.

Further losses of electricity are certainly also caused in the accumulator by the acid about the electrodes becoming saturated with oxygen or

[1] Zeitschr. f. Elektrochem. III, p. 662. 1897.

hydrogen, which gases diffuse to the opposite electrode, oxidizing or reducing the same, thereby bringing about a self-discharge of the cell. It goes without saying that the oxygen of the air also effects a gradual oxidation (discharge) of the lead sponge. As is well known, the free access of air brings this about very rapidly, and is accompanied by a strong heating of the lead sponge.

The last modes of self-discharge considered can only cause slight losses of current, since they depend upon the slow-acting phenomenon of diffusion, and are therefore practically of considerably less importance than those first mentioned.

In conclusion it should be noted that the acid density is of great influence upon the rate of self-discharge of the lead-sponge electrode. During spontaneous discharge hydrogen is liberated on the impurities; that is, these play the part of hydrogen electrodes and the self-discharging must therefore, in accordance with the electromotive forces contained in Table VIII (p. 79), greatly increase with the acid concentration. With very concentrated acid the E.M.F. of the combination Pb—H_2 exceeds 0.64 volt (see table above), the value of the evolution potential of hydrogen on a lead surface; in concentrated acid, therefore, even the purest lead must dissolve of its own accord with a copious evolution of hydrogen. This conclusion, as is well known, is confirmed by actual experience.

Measurements on the rate of self-discharge with varying concentrations of acids have not been

made, but practical experience with accumulators has shown, in agreement with the above, that self-discharge increases very greatly with the concentration of the acid.

(*c*) *Sulphatization.*—If we attempt to recharge an accumulator that has stood for some time in a discharged condition, we find that the internal resistance has very greatly increased; the resistance does not begin to diminish until the charging current has passed through the element for some time; in the course of the charging it slowly approaches the normal value. A capacity test shows that the capacity of the cell has suffered greatly. Standing in a discharged condition is therefore exceedingly detrimental to an accumulator, and it requires several chargings, dischargings, and overchargings to bring it back again to its former serviceability. If discharging has been very complete and the cell has been in this condition for several weeks, it is possible to make the impaired plates serviceable again only with the aid of a very great quantity of electricity, so that it is usually cheaper to replace them by new ones.

If we observe carefully the plates of an accumulator which has been strongly discharged and allowed to rest, we notice that their color gradually becomes lighter. After a number of days small white spots appear in isolated places, which increase in size from day to day, so that after a number of weeks the plates appear completely covered with a white coat.

A careful testing of this coat shows that it consists of pure lead sulphate; for that reason the phenomenon described, so detrimental to the accumulator, has been given the ill-chosen name "sulphatization of the plates."

We have seen in the foregoing chapters that with every normal discharge lead sulphate is formed on both electrodes, which is without the slightest difficulty changed back into peroxide and lead during charging. At first glance this fact seems to stand in contradiction to the phenomenon of so-called sulphatization; the assumption therefore has frequently been made that during normal discharge the lead sulphate forms in an allotropic modification of the ordinary sulphate, which only after some time converts into the latter and causes the phenomenon of sulphatization. We know, however, no such modification of lead sulphate or any other similarly constituted salt; the assumption of such a sulphate is therefore entirely arbitrary, and besides it is by no means necessary for the explanation of the phenomenon in question.

Sulphatization can, as was shown by Elbs,[1] be very simply explained in the following way: During the discharge of the accumulator there is formed on every lead or peroxide particle a thin layer of very finely divided lead sulphate saturated with acid. If the accumulator is allowed to stand in this condition, it is exposed to slight temperature

[1] Die Accumulatoren, p. 40. 1896.

fluctuations, which cause the sulphate to draw together into larger, isolated crystal crusts. With a rise in temperature the solubility of the sulphate greatly increases, therefore the smallest crystals present will entirely pass into solution. With a slow cooling following upon this, the crystals still present will increase in size, so that the fluctuations in temperature result in a continued growing of the large crystals at the expense of the small ones, whereby the active mass is finally covered with an impenetrable layer of sulphate crystals. The greater solubility of the small crystals also acts in the same direction (see Ostwald, Analytical Chemistry). The increase of the internal resistance which comes about in this way can also frequently be observed in the case of other elements working with solid salts, especially in the Clark and Weston elements.

The growing of the sulphate coat naturally causes the color of the active mass lying under it to be covered more and more, and the plates assume a white color. As a matter of course, with the small solubility of the lead sulphate the larger sulphate crystals are not so accessible to the action of the charging current, as finely divided sulphate masses mixed with conducting lead or peroxide particles.

We shall now attempt to determine the conditions through which the disturbing sulphatization can be most effectively reduced.

As demonstrated by the experience of the accumulator factories and the measurements of Heim,

the sulphatization increases rapidly with the acid density. This fact is very easily understood in the light of the above. Evidently the rate of re-crystallization must likewise increase greatly with the solubility of the sulphate; now the solubility of a lead salt at first decreases upon adding an acid having an ion in common with it, but upon further addition the same increases again, in that the acid forms complex compounds with the salt.

In Fig. 14, for example, are given the solubilities

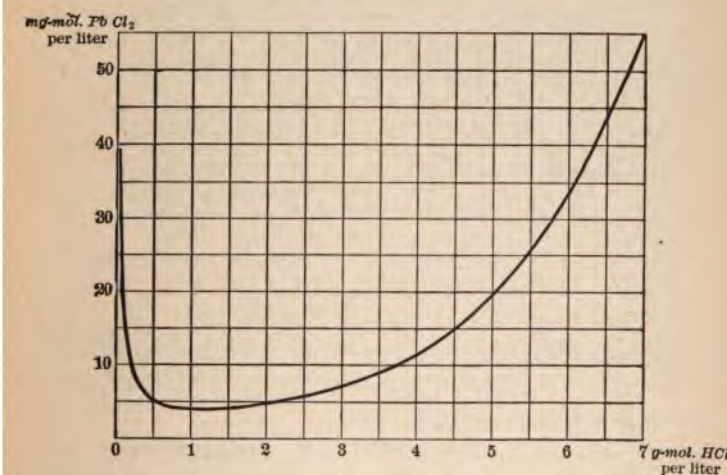

FIG. 14.

of lead chloride in water with the addition of varying amounts of hydrochloric acid, as recently very accurately determined by v. Ende.[1] The solubility

[1] Inaug.-Diss. Goettingen 1899 and Zeitschr. f. anorg. Chem. 26, p. 129 (1901).

of the lead chloride reaches a minimum at about 1 normal acid, rapidly increasing upon further addition of acid to a value four times as great as that in pure water.

Unfortunately the solubility curve for lead sulphate in varying concentrations of sulphuric acid has not as yet been determined; I have been able to find in the literature only the determinations given in Table XV.

TABLE XV.

Acid Density.	Per Cent H_2SO_4.	$PbSO_4$ in Grams per Liter.	Temperature.	Observer.
1.000	0	0.042	11° C.	Fresenius
1.000	0	0.046	18° C.	F. Kohlrausch & Rose
1.00	about 1	0.027	—	Fresenius
1.22	29	0.012	—	Gladstone and Hibbert
1.54	64	0.046	—	Kolb
1.79	86	0.197	—	Kolb
1.84	99	0.72		Kolb

The graphic representation of these values shows (Fig. 15) a course quite similar to the solubility curve for lead chloride.

This lead sulphate curve can of course make no claim to accuracy, since the values are taken from different observers. There still remains a piece of work, important to the theoretical as well as the practical side of the accumulator, to determine this curve accurately (especially the dotted portion).

As far as can be seen from these measurements, the minimum of solubility of lead sulphate, and

therefore that of sulphatization, seems to lie near 1.5 g.-mol. H_2SO_4 (13 to 14 per cent H_2SO_4). This would agree very closely with the observations of

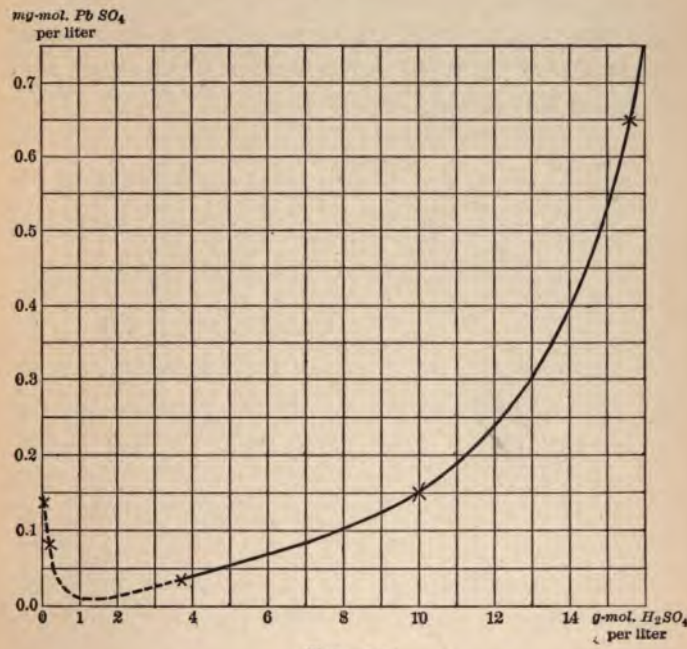

FIG. 15.

Heim, according to which, in order most effectively to keep up the capacity of a cell, it is best to fill the same with 16 per cent H_2SO_4, measured in the normally discharged condition. With an acid of 5 g.-mol. H_2SO_4 (38 per cent) the solubility has reached an amount ten times, and with a con-

centration of 15 g.-mol. (83 per cent) one hundred times, as great as that in 14 per cent acid.

From this it is very apparent how greatly the sulphatization is influenced by the acid density, and how detrimental it is to allow a discharged accumulator to stand for a longer time in an acid which is too strong or too weak.

XI.

INTERNAL RESISTANCE.

THE internal resistance [1] of the accumulator, thanks to the good conductivity of sulphuric acid, is extremely small, even in the smallest forms used (accumulators for measuring purposes), amounting to only several hundredths ohm, and falling to a few ten-thousandths ohm in the larger cells. The loss of voltage caused hereby is consequently also slight and with the permissible maximum current density amounts to a few hundredths volt, so that the loss of energy in the cell due to heating comes to only about 2 to 5 per cent of the entire output of the accumulator. That is, practically the internal resistance is of little importance, especially as it seems entirely out of the question to construct an accumulator with a markedly smaller resistance. In spite of this, the careful investigation of this magnitude, and in particular its variation with the passing of current, naturally possesses great theoretical interest.

The least faulty investigations in this direction

[1] For methods of measurement compare closing chapter.

we owe to Haagn,[1] who studied the internal resistance of the accumulator, by means of a method devised by Nernst, in the open condition as well as during the withdrawal of different amounts of current.

In the first place Haagn tested whether the strength of current had any influence, at a certain phase of the charging or discharging, upon the internal resistance. For this purpose a small accumulator (Pollak) of about 2 amp.-hr. capacity was discharged to 1.7 volts and then varying current-strengths withdrawn. The results were:

Current-strength in Amperes.	Resistance in Ohms.
0	0.0422
0.1	0.0421
0.2	0.0423
0.48	0.0423
0.65	0.0423
1.0	0.0423
0	0.0422

The resistance is as good as entirely independent of the intensity of the current. The same result was obtained with a half-discharge of the accumulator, the resistance being constantly 0.0187 ohm, i.e., about one half as great. These measurements show that the resistance increases in the course of the discharge. This is still more apparent from Fig. 16, which represents the variation in

[1] Inaugural-Dissertation, Goettingen, 1897. Zeitschr. f. physikal. Chem. XXIII, Heft. 1. 1897.

resistance of the same cell during the discharge with 0.65 ampere.

During charging the resistance recedes in the same way as it rose during discharge, as a glance at the

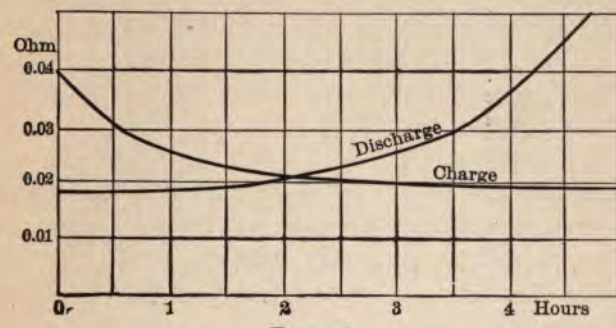

FIG. 16.

second curve of Fig. 16 shows, which pertains to a charging with 0.52 amp. This behavior of the resistance during charging and discharging Haagn also found with cells of different construction, showing that it is typical of the lead accumulator.

The decrease of the resistance during charging and the increase of the same during discharge was first discovered by Hallwachs,[1] and later was also observed by Haeberlein [2] and Boccali.[3] The measurements of Hallwachs, carried out according to the method of F. Kohlrausch with alternating current and telephone, are contained in Table XVI.

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[1] Wied. Ann. 22, p. 95. 1884.
[2] *Ibid.* 31, p. 402. 1887.
[3] Elektrotechn. Zeitschr. 1891, p. 51.

TABLE XVI.

Charge.		Discharge.	
Time in Hours.	Resistance in Ohms.	Time in Hours.	Resistance in Ohms.
0	0.30	0	0.008
0.5	0.03	2	0.01
1	0.02	4	0.012
2	0.01	10	0.09
4	0.008	13	0.25

The changes of the resistance are here considerably greater than in the case of Haagn's measurements, which is probably explained by the fact that in the older elements employed by Hallwachs the contact between the active mass and the carrier was not as perfect as in the present plate construction; and besides in the investigations of Hallwachs the cell was considerably more strongly discharged.

The measurements of Haeberlein are of a qualitative nature. Boccali obtained the following values for the resistance of a large cell during charge and discharge, measured in closed circuit after a method to be discussed later:

Charge.		Discharge.	
After 2 hours.....	0.0017 Ω	At beginning.....	0.0022 Ω
" 4 "	0.0015 "	After 1 hour.....	0.0025 "
" 5 "	0.0022 "	" 3 hours.....	0.0028 "
" 6 "	0.0024 "	" 4 "	0.0030 "

In a general way these measurements agree with the results of Hallwachs and Haagn. Boccali finds, however, that at the close of the charging

with the beginning of the evolution of gas the resistance, which fell at first, rises again. Haagn observed no such rise in the resistance; the same is very plausible, however, since an increase in resistance is usually observed on electrodes evolving gases; probably the overcharging was not sufficiently prolonged in Haagn's investigations.

The cause for the decrease of the internal resistance with the charge and the increase with the discharge is evidently chiefly to be looked for in that during the discharge of the cell the conducting lead and peroxide particles become more and more densely covered with a layer of non-conducting lead sulphate. In addition to this, the sinking of the acid density during discharge brings about a gradual rising of the resistance; the variations of the acid concentration appearing at the electrodes affects the resistance in the same direction.

That, however, the variations in concentration at the electrodes have only a slight influence on the resistance of the cell is demonstrated by a comparison of the variation of resistance with slow and rapid discharge, which was carried out by Haagn and is contained in the accompanying figures:

Rapid Discharge (0.65 Amp.).	Slow Discharge (0.27 Amp.).
0.0177 ohm	0.0165 ohm
0.0184 "	0.0171 "
0.0193 "	0.0181 "
0.0213 "	0.0206 "
0.0261 "	0.0251 "
0.0516 "	0.0475 "

The resistance values given in both columns pertain to the same number of ampere-hours withdrawn. In the case of the slow discharge the resistances are, in consequence of the slight decrease in the concentration of the acid at the electrodes, a little smaller all the way through than with the rapid discharge.

There still remains to be discussed the question as to how the variations in resistance distribute themselves between the two electrodes. Haagn likewise made measurements pertaining to this. He discharged the individual electrodes against amalgamated zinc plates and at the same time determined the resistance of the combination. The values given show clearly that the measurements are greatly influenced by resistance variations at the zinc electrode and therefore do not permit of any certain conclusion as to the individual electrodes; I therefore refrain from giving them here. It remains as a promising problem to investigate the resistance variation of the individual electrodes during the passing of current against a third electrode without current

XII.

CAPACITY.

(*a*) *General.*—By capacity of an electric accumulator we understand the amount of current (expressed, let us say, in ampere-hours) which can be taken from the same until we reach complete exhaustion. When discharging with very weak current it is evidently determined, according to Faraday's law, by the weight of the active mass, in that 3.86 g. lead sponge and 4.45 g. lead peroxide upon conversion into sulphate can give an amount of current equal to 1 amp.-hr. This ideal capacity is, however, never attained in actual practice, because during discharge with stronger currents the voltage of the cell, in consequence of the disappearance of acid from the electrolyte (compare Chapter VIII), goes down to zero, while there is a large excess of active mass left.

Therefore with the customary current densities of discharge only a small fraction of the active mass is utilized in the production of current. In addition it is impossible in practice completely to discharge the accumulator, since the current must

be sent into the external circuit with constant voltage, and entire discharge would also be very detrimental to the cell. One is compelled, therefore, to interrupt the discharge at the point of the beginning of the rapid falling off of the voltage (see Fig. 7), and it has been agreed to define the capacity of a storage battery, in the technical sense, as that quantity of electricity (expressed in ampere-hours) which the same can deliver until its pole-potential has decreased by one tenth of the original value—say, for instance, from 2 to 1.80 volts, or from 1.96 to 1.77 volts.

The circumstance that it is possible to utilize only a fraction of the active mass for the production of current is caused, as follows from the discussions of Chapters VIII and IX, by the fact that in discharging with stronger currents the acid is unable to penetrate rapidly enough into the active mass. That we have to deal here essentially with an acid shortage is cleverly demonstrated by the following experiment devised by Liebenow.[1]

Liebenow soldered a negative accumulator-plate P (grid-plate), so as hermetically to close a window-like opening in the side of a leaden box K (Fig. 17). In this box he suspended a peroxide plate P', placed the whole into a second, larger vessel, and filled both with acid to the same level. Now the plate was discharged with a constant current of 8 amp. and its capacity determined by measuring

[1] Zeitschr. f. Elektrochem. IV, p. 61. 1897.

the potential difference against zinc. The capacity found was 14.4 amp.-hr. After renewed charging, the level of acid in the box *K* was kept considerably higher during the second discharge, so that acid was continually pressed through the plate. The capacity now was 41.6 amp.-hr., i.e., almost three times as great.

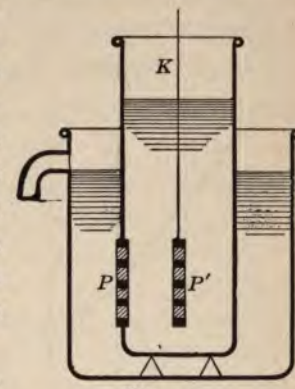

FIG. 17.

The phenomenon of recovery considered in Chap. X shows plainly that the small capacity is brought about by a shortage of acid in the electrode mass. This same circumstance also causes the capacity to diminish greatly with the intensity of the discharge current, along with its great susceptibility to acid density, electrode thickness, and temperature. As was pointed out on p. 124, the changes in concentration are considerably greater at the peroxide than at the lead-sponge electrode (a 1.6 times greater reduction at the former than at the latte). From this it follows that the capacity of the peroxide plate must be less than that of the sponge plate made of an exactly similar paste, as can be seen from the discharge curves Fig. 11 (p. 127). We shall next consider, somewhat more in detail, these variatons of the capacity and their causes.

(*b*) *Influence of Strength of Discharge Current.*— The decided diminution of the capacity of a storage cell with increasing intensity of the discharge current is shown by the continuous curve of Fig. 18,[1]

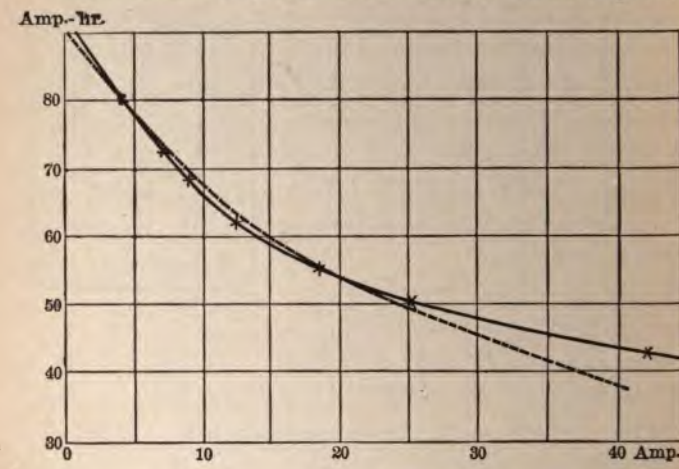

FIG. 18.

in which the current-strengths in amperes are plotted as abscissæ and the corresponding capacities in ampere-hours as ordinates. A raising of the intensity of discharge from 4 to 40 amp. reduces the capacity by one half.

Various empirical formulæ have been proposed for a rapid, approximate calculation of the capacity for a definite taxation, which give with a greater or less degree of accuracy the course of the capacity curve and are of importance to the practical calcu-

[1] Taken from the measurements of C. Liebenow. Zeitschr. f. Elektrochem. IV, p. 61. 1897.

lation of the serviceability of storage cells. Schroeder [1] found that the capacities of the accumulators of the Hagen factory are approximately given for rapid discharge by the equation

$$K \cdot \sqrt[3]{I^2} = m, \quad . \quad . \quad . \quad . \quad (52)$$

in which K stands for capacity, I for current-strength of discharge, and m a constant characteristic of the particular cell.

This equation has the advantage over the following ones in that it contains only one constant, and therefore it is only necessary to make one capacity test in order to be able to draw the curve. It is, however, applicable to only a limited interval for I, which it is true is seldom exceeded in actual practice, so that the usefulness of the equation is hereby little affected. For weaker discharge currents, however, it gives altogether erroneous results in that as the values of I converge toward zero it gives infinite capacities. Liebenow [2] has therefore, in the case of slow discharge, replaced Schroeder's equation by the following:

$$K = \frac{M}{1 + aI}, \quad . \quad . \quad . \quad . \quad . \quad (53)$$

in which K and I are the same as before and M and a are constants. This equation is especially applicable to weak currents; one is compelled,

[1] Elektrotechn. Zeitschr. 1894, p. 587.
[2] Zeitschr. f. Elektrochem. III, 1896, p. 71.

however, to make two capacity measurements with different strengths of current in order to determine the two constants.

Combining equation (53), holding for weak discharges, and (52), for strong discharges, we get, as Liebenow [1] has shown, an equation applicable to a much wider range:

$$K = \frac{A'}{1 + \frac{a}{t^n}},$$

in which A', a, and n are constants. Liebenow found that n is always equal to very nearly 0.5, so that only the constants A' and a remain to be determined for each individual accumulator. Therefore

$$K = \frac{A'}{1 + \frac{a}{\sqrt{t}}}. \quad . \quad . \quad . \quad . \quad . \quad (54)$$

In Table XVII a comparison is given between the values of K as obtained by means of this equation and the measured capacities, $A' = 104.326$ and $a = 1.478$ being the values of the constants used.

In view of the uncertainty to which capacity measurements are subject, the agreement between the measured and calculated values is extremely satisfactory. It is true that upon doubling the intensity, for instance, greater discrepancies appear.

[1] Zeitschr. f. Elektrochem. IV, 1897, p. 58.

TABLE XVII.

Duration of Discharge, t Hours.	Discharge Current, i Amperes.	Capacity, K.		Difference.
		Observed.	Calculated.	
1	42.5	42.5	42.2	+0.3
2	25.3	50.5	50.1	+0.4
3	18.5	55.5	56.2	−0.7
5	12.4	62	62.8	−0.8
7½	9.1	68	68.2	−0.2
10	7.2	72	71.2	+0.8
20	4.0	80	79.5	+0.5

Recently Peukert [1] also carried out extensive investigations upon the relation of the capacity to the time of discharge. The following values were obtained with a Correns battery:

Discharge Current in Amperes.	Duration of of Discharge in Hours.	Capacity in Ampere-hours.
10	19.8	198
15	9.75	146
18	8.5	153
20	6.5	130
27.2	4.41	120
30	3.67	110

These figures satisfy the equation

$$I^n t = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (55)$$

when we place $n = 1.47$.

For a number of other accumulator systems the following values for n were obtained:

[1] Elektrotechn. Zeitschr. 1897, p. 287.

System.	Type.	Value of n.
Acc.-Fabr.-A.-G. (Tudor) ...	E	1.35
" ...	E S	1.48
Pollak	S K	1.36
"	R	1.51
Correns	H	1.72
"	Q	1.64
G. Hagen	A	1.39
"	B	1.39
De Khotinsky	N	1.55
"	X	1.55
Gülcher	A	1.38
"	C & E	1.36

By means of these constants and equation (55) we get durations of discharge which agree well with the measured values.

If we introduce the capacity $K = It$ in place of t, the duration of discharge, we obtain for the capacity K_1 and the current-strength I_1 the value

$$K_1 = K\left(\frac{I}{I_1}\right)^{n-1},$$

when K is the capacity for the current I.

For the particular case in which n has the value 1.66 this equation becomes identical with the one given by Schroeder (equation 52). Later Loppe[1] carefully tested Peukert's equation on a great number of types, resulting in a good confirmation.

Equations (52), (53), (54), and (55) apply only for discharge with constant current, a condition seldom

[1] Assoc. des Ingénieurs-Electr. H. 11. 1898. Elektrotechn. Zeitschr. 1898, p. 146.

fulfilled in the practical use of an accumulator. Farther on we will meet with an equation which also permits the calculation of the capacity with variable taxation, but before taking that up we shall attempt to account theoretically for the course of the capacity curve.

For this purpose we shall follow more closely the changes within the active mass. The substance of the plates consists of solid conducting material, permeated with fine pores. As soon as the discharge current is closed, the active mass begins to withdraw acid from the electrolyte for the formation of sulphate. The concentration within the pores therefore falls off rapidly and continues until the difference in concentration with respect to the outer acid has become so great that the equalization of concentration by diffusion just counterbalances the consumption of acid. That is, the quantity of acid diffusing inward per unit of time must at every moment be equal to the quantity consumed by the current.

From this point of view it is easy, with the aid of the diffusion law of Fick, to develop a relation between capacity and strength of current, which at least holds approximately for small intensities.

Let c_a stand for the concentration of the outer acid, c_i for the variable concentration within the pores; then for small differences we can set the quantity of acid diffusing as approximately proportio
difference $(c_a - c_i)$. In a

tional to the diffusion coefficient D, the cross-section of the pore q, and inversely proportional to the length of the pore l. We get as the expression for S the amount of acid diffusing into the pore in one second,

$$S = \frac{D \cdot q(c_a - c_i)}{l}.$$

The amount of acid S' consumed by the current per second is proportional to the current strength I, i.e.,

$$S' = \text{const. } I.$$

Since for the stationary condition S must equal S', it follows that

$$\text{Const. } I = \frac{D \cdot q(c_a - c_i)}{l}. \quad . \quad . \quad . \quad (56)$$

Upon closing the current electrolysis begins in the outer layers of the active mass and penetrates into the interior, proportional to the amount of current withdrawn. The depth of the pores coming into question is therefore to be taken proportional to the quantity of current (It) withdrawn:

$$l = \text{const. } I \cdot t.$$

In addition, during the course of discharge, the cross-section q of the pores diminishes considerably, in that in place of the lead peroxide and sponge

more and more lead sulphate appears, which occupies a considerably greater volume (see Table XIV, p. 103). This change also takes place proportional to It. If the cross-section at the beginning of discharge is q_0, then at the end of the time t it has decreased

$$q = q_0 - \text{const. } I \cdot t.$$

At the end of discharge the E.M.F. has decreased a definite amount, about 0.20 volt, and the concentration difference $(c_a - c_i)$, which can easily be calculated, has reached a definite value, the same for all capacity measurements. Here it suffices to know that $(c_a - c_i)$ has the same constant value at the end of discharge for all measurements. Substituting this result and the above values of q and l in equation (56), we obtain

$$I^2t + AIt = B,$$

in which A and B are constants. Now the capacity is

$$K = It,$$

and we obtain for the capacity at the current-strength I the equation

$$K = \frac{B}{A + I}.$$

This equation is identical with equation (53), empirically derived from the measurements by Liebenow.

In Fig. 18 the dotted curve gives the capacities as calculated by this equation when the values $A = 28.9$ and $B = 2632$ are used. The calculated curve fits very well to the measured one in the case of the smaller intensities. With greater current-strengths very marked deviations appear, which are probably due to Fick's diffusion law being applicable to electrolytes only when the concentration differences are small, and this condition is no longer fulfilled when discharging with stronger currents.

As previously mentioned, above discussions and equations pertain to discharge with constant current, a condition seldom fulfilled in the technical application of an accumulator. The theoretical treatment in the case of discharge with variable current strength has been successfully taken up by Liebenow.

The amount of current K_t which can still be taken from an accumulator, after the same has been discharged for some time with the current i, can be expressed by the equation

$$K_t = K_{\max.} - \int_0^t i\,dt - \int_0^t dk_t, \quad . \quad . \quad (57)$$

in which $K_{\max.}$ is the maximum capacity which could be obtained by discharge with a very weak current. The member $\int_0^t i\,dt$ represents the amount

of current already withdrawn at the time t. The summation $\int_0^t dk_t$ may be termed the latent contents of the accumulator. The same accounts for the circumstance that one cannot get the maximum capacity when discharging with stronger currents; it is not liberated until the cell has had time to recuperate. The same disappears upon discharging with very weak current. The small latent content dk_t is dependent upon the time dt during which the current i has acted; it is a function $\phi(i)$ (unknown for the present) of the current strength, and thirdly, a function $f(\tau)$ of the time which has elapsed since the beginning of the discharge. We can therefore write

$$dk = \phi(i) \cdot f(\tau) dt,$$

from which follows

$$K_t = K_{\max.} - \int_0^t [i + \phi(i) f(\tau)] dt. \quad . \quad . \quad (58)$$

For the determination of $\phi(i)$ and $f(\tau)$ we can use the above empirical relations (equation 54) for discharge with constant current strength. Upon complete discharge with constant i, $K_t = 0$, i, and $\phi(i)$ are constant, and for τ we must introduce t; equation (58) then takes the form

$$0 = K_{\max.} - it - \phi(i) \int_0^t f(t) dt,$$

or

$$it = \frac{K_{\max.}}{1 + \frac{\phi(i)}{i} \frac{1}{t} \int_0^t f(t)dt}.$$

Written in this form this equation is entirely similar to the empirically found equation (54). A comparison with the latter at once gives

$$\frac{\phi(i)}{i} \frac{1}{t} \int_0^t f(t)dt = a \cdot t^{-0.5}.$$

Putting $\frac{\phi(i)}{i} = c$, we get

$$\int_0^t f(t)dt = \frac{a}{c} t^{0.5}.$$

Differentiation gives

$$f(t) = \frac{a}{2c} t^{-0.5},$$

or, since t was exchanged with τ,

$$f(\tau) = \frac{a}{2c\sqrt{\tau}}.$$

Substituting the values of $\phi(i)$ and $f(\tau)$ finally gives the expression

$$K_t = K_{\max.} - \int_0^t \left(1 + \frac{a}{2\sqrt{\tau}}\right) i dt, \quad . \quad . \quad (59)$$

whose constants are to be obtained by means of equation (54) from discharge tests with constant current. For the case that i as a function of t is known, the integration can be carried out; in practice this is, however, seldom true, and we have to split up the discharge into a larger number of separate discharges and calculate each separately.

If we wish to use the equation to determine the size of the element for a given taxation, we must first determine the constants $K_{max.}$ and a for 1 sq. dm. of surface of the kind of plate to be employed. For the desired surface, then, of, say, n sq. dm. we must introduce into the calculation $K_{max.}$ n times greater and an times smaller.

If the values of the constants are referred to 1 sq. dm. $K'_{max.}$ and a', then we have for the entire element, since with complete discharge $K_t = 0$,

$$0 = nK'_{max.} - \int_0^t i\,dt - \frac{a'}{2n}\int_0^t \frac{i}{\sqrt{\tau}}dt. \quad . \quad (60)$$

If we now calculate from the given taxation the values of

$$\int_0^t i\,dt = B \quad \text{and} \quad \frac{a'}{2}\int_0^t \frac{i}{\sqrt{\tau}}\cdot dt = C$$

and introduce these into the equation

$$n = -\frac{1}{2}\frac{C}{A} + \sqrt{B + \frac{1}{4}\left(\frac{C}{A}\right)^2},$$

which follows directly from equation (60) ($K_{max.} = A$), we get the number of square decimeters of plate surface which the element must have for the given taxation.

(*c*) *Influence of Thickness of Plate.*—It follows directly from the discussion in the previous section that the thickness of the active layer must also be of great influence upon the capacity. If the active substance is distributed in a thin layer with large surface, the acid can more easily penetrate into the plate than when the active material is in the form of a thick plate with a small surface. Therefore elements with thin plates have a considerably greater capacity than such of like weight but thick electrodes.

Liebenow found that the influence of the thickness of plate is approximately expressed by the equation

$$K = \frac{M'}{1 + a' I \cdot d},$$

in which M' and a' are constants, I is the current-strength, and d the thickness of plate. Just as equation (53), this one can also be derived from the diffusion process in the electrode substance.

Unfortunately, very thin plates, as a result of the deeper penetration of the action of the current, are short lived, so that they cannot be employed in practice.

(*d*) *Influence of the Acid Density.*—The influence of the acid density upon the capacity of a storage

battery was first investigated in detail by Heim.[1] A Tudor accumulator and a storage-battery of the Electrical Power Storage Company (Julien, Huber) were successively filled with acids of varying density, charged and discharged a number of times, and then subjected to a capacity measurement. The results of the investigation are contained in Fig. 19. The acid densities given are measured after discharge. The capacity rises rapidly with increasing acid concentration, reaches a maximum at a density of 1.1 (16 per cent), and again falls off strongly at greater density

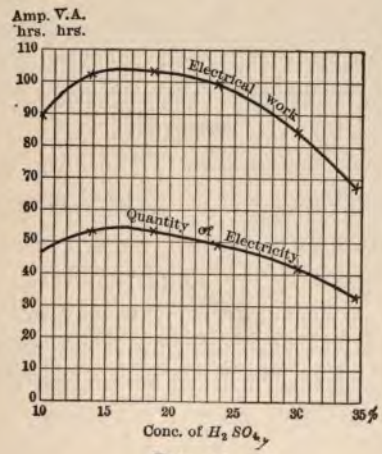

FIG. 19.

Recently Earle [2] carried out measurements upon the influence of acid concentration upon capacity,

[1] Elektrotechn. Zeitschr. X, H. 4. 1889.

[2] Zeitschr. f. Elektrochem. II, p. 559. 1895–96.

using plates 6 mm. and 10 mm. thick. The observed capacities are given in Fig. 20.

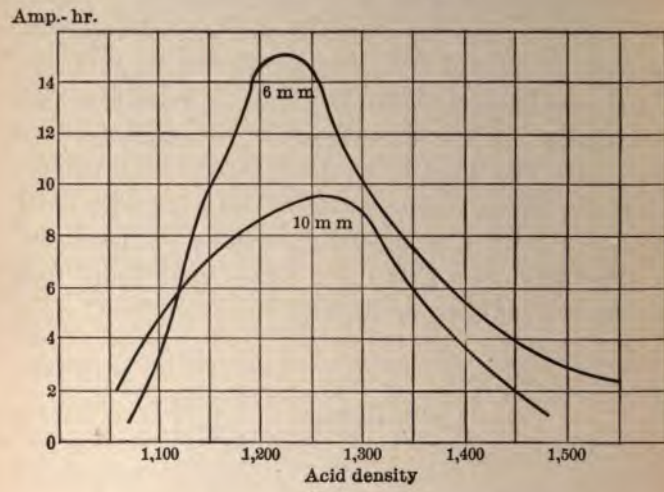

FIG. 20.

The capacity maximum is also very marked in these measurements, lying, however, at a density of from 1.22 to 1.27 (30 to 34 per cent), i.e., noticeably higher than in Heim's measurements. This displacement of the maximum is probably due to the fact that Earle allowed the discharge to follow immediately upon the charge, while Heim did not make the measurements until the accumulator had stood charged for from 15 to 18 hours. However, with an acid of over 20 per cent H_2SO_4, according to the observations of Heim, the amount of the discharge falls off noticeably with the time between the end of the charge and the beginning

of the discharge, as a result of sulphatization (see Chapter X). This falling off is greater the more concentrated the acid. Schenek also found that the capacity of his storage-battery was greatest when the acid had a density from 1.22 to 1.25.

The question arises, how the behavior of the capacity with the variation of the acid density, as pictured in Figs. 19 and 20, is theoretically to be explained. According to the discussions in Chapter VIII one would expect the capacity to rise continuously with increasing acid density. It is to be assumed, from the first, that with higher concentrations (above 40 per cent) the increased self-discharge, and especially the sulphatization, will be a hindrance to the increase in capacity, but still this influence is not sufficient by far to explain the decided falling off of the curves above the density 1.22. The capacity maximum may more likely come about in the following manner:

At the beginning of discharge the lines of current first enter principally the outer layers of the active mass, where they find the least resistance. In the same measure as the concentration polarization develops at the outer layers, the current lines penetrate deeper and deeper into the electrode, and in such density that everywhere in the pores the loss of potential ($I \cdot R$) is equal to the polarization prevailing in the outer layers. This condition must necessarily be fulfilled, since the active mass (lead as well as lead peroxide) is a first-class conductor, and therefore must have the

same potential within the pores as without. If the polarization at the outer layers has reached the value of 0.2 volt, the potential of the accumulator has fallen at the same time by 0.2 volt and the discharge is interrupted. At this moment the lines of current have penetrated so far into the active mass that the loss of potential in the pores, that means the product of current strength and pore resistance (I·R), has likewise reached the value of 0.2 volt. Now the resistance of the pores is determined by the conductivity of the sulphuric acid filling them; the product I·R herewith will reach the value 0.2 later, giving a greater capacity the better conducting the acid is which fills the pores.

As is well known, the conductivity of sulphuric acid at first increases with concentration, attains a maximum at 30 per cent H_2SO_4 (density 1.224), and then decreases again. According to the above discussion, then, the capacity must reach a maximum at a density of 1.224, as the above measurements splendidly confirm.

(*e*) *Influence of Temperature.*—The discussions in the section just preceding show clearly that the conductivity of the electrolyte determines the capacity of a storage battery; from which it follows directly that the temperature must also have great influence, because the conductivity is in a high degree dependent upon the same. According to the measurements of F. Kohlrausch, the conductivity of 20 per cent acid increases by about 1.5 per cent per degree rise in temperature.

Consequently the capacity must likewise increase very greatly with rising temperature, inasmuch as diffusion is also greatly accelerated at the same time. Fig. 21 gives discharge curves of a cell at 15 and 37 degrees.[1]

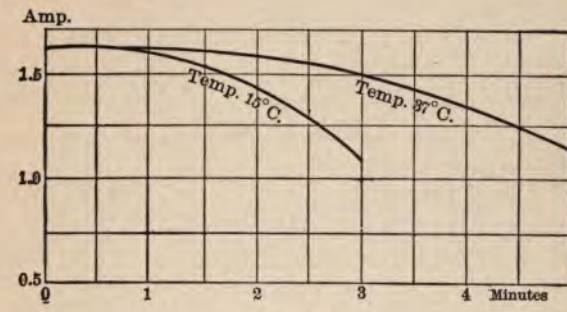

FIG. 21.

The cell was discharged into a constant resistance, so that the given current-strengths are approximately proportional to the pole-potential of the cell. Raising the temperature 22° increases the capacity by about 50 per cent; so the influence of temperature is in fact exceedingly great. The raising of the E.M.F. due to increase in temperature is, in the case of the density of acid usually employed, so small that its influence on the capacity is negligible.

[1] Taken from the measurements of Gladstone & Hibbert. Elektrotechn. Zeitschr. 1892, p. 436.

XIII.

DEGREE OF EFFICIENCY AND WORKING EFFICIENCY.

In the preceding chapter we considered the capacity of a storage battery with varying current taxation and external conditions, and the question as to the ratio of the amount of current and electrical work during discharge to the quantity of current or work required to charge, i.e., how high is the efficiency, still remains to be answered.

Here it is necessary to distinguish between efficiency as to quantity of electricity and efficiency as to electrical work. The first is usually termed degree of efficiency ("Wirkungsgrad"), and is expressed by the quotient of the quantity of current, measured in ampere-hours, obtained during discharge, to the quantity of current passed in during charging. Indicating the degree of efficiency by G, the charge and discharge current-strength by I_l and I_e respectively, the time of charge and discharge by t_l and t_e respectively, then

$$G = \frac{I_e t_e}{I t_l},$$

or, in case of the current varying with the time,

$$G = \frac{\int_0^{t_e} I_{t_e} dt}{\int_0^{t_l} I_t dt}.$$

G is always less than 1, but in practice, with anything like reasonable charging, a degree of efficiency of from 0.94 to 0.96 is obtained. The slight losses of current, amounting to from 4 to 6 per cent, come from self-discharge, and especially from the gas evolution, which is difficult entirely to avoid when charging with stronger currents.

The degree of efficiency decreases only slightly with increasing acid density and strength of current, and not until we reach a very high current density is a noticeable fraction of the current consumed for gas formation. The extent of the same is essentially determined by the purity of the materials used in the construction of the accumulator; by using acid contaminated with platinum salts the degree of efficiency can go down to 0.3 and less.

Of considerable greater importance in practice than the degree of efficiency is the working efficiency ("Nutzeffekt"), as it may be termed, which represents the ratio of the work gained in the outer circuit, to the electrical work required between the poles of the storage battery in charging it. Retaining the same symbols for current-strength

and time as above, and indicating the pole-potential of charge and discharge by K_l and K_e, we get as the expression for the working efficiency

$$N = \frac{\int_0^{t_e} K_e I_e dt}{\int_0^{t_l} K_l I_l dt},$$

or if charge and discharge is carried out with constant and equal intensity, then

$$N = \frac{\int_0^{t_e} K_e dt}{\int_0^{t_l} K_l dt}.$$

The values of these integrals are represented by the surface, which charge and discharge curve enclose with the axis of abscissa and ordinate (see Fig. 7, p. 108); the ratio of these surfaces represents the working efficiency, and the difference of the same, i.e., the portion of the surface included between the two curves, the loss of energy which accompanies the storage in the accumulator.

The working efficiency is 0.75–0.85 (75–85 per cent), even though we recover during discharge, as we just saw, almost the entire amount of current put in during charging. That is, the energy loss is almost entirely caused by the difference between the charge and discharge potential, or in other words by the concentration polarization produced

at the electrodes. The loss of voltage as a result of the internal resistance is, thanks to the smallness of the latter (see Chap. XI), exceedingly slight, seldom amounting to more than 3 per cent with the usual acid and current density.

The heat which appears in the cell as a result of the loss of work is not produced according to Joule's law, but is heat of dilution, resulting from the continual equalization of the acid layers of different concentration.

The mixing of the acid of different concentrations comes about chiefly through diffusion, partly also through convection, and in small part, especially after interrupting the current, through concentration currents of the kind described on p. 82. In order to get a conception of the influence which current strength and acid density have upon the loss of energy, we shall leave out diffusion and convection and consider the equalization of concentration as essentially brought about by local concentration currents. Then the amount of work consumed by the accumulator current in producing and keeping up the concentration difference must be equal to the work which it is possible to gain in maximum through the equalization by local currents.

The energy loss ε in the accumulator is therefore to be taken equal to the quantity of heat produced by the concentration currents; herewith at once

$$\varepsilon = i^2 r t \text{ volt-coulombs},$$

where i represents the sum of the current strengths, r the sum of the resistances, and t the time in seconds of all the concentration currents in the plates. The resistance r is made up of the resistance of the substance of the plates and the acid contained in the pores. Since the former is so small as to be negligible compared with the latter, we can write

$$r = \frac{\gamma}{k},$$

where γ is the resistance capacity of the pores of the plates and k the mean conductivity of the acid in the substance of the electrodes; that is,

$$\varepsilon = \gamma \frac{i^2 t}{k} \text{ volt-coulombs.}$$

Now with an accumulator current of constant strength the E.M.F. is also constant, and therefore the concentration difference in the plates must have a constant value; that means that through the local concentration currents the acid is replaced or carried away just as rapidly as it is consumed or formed by the accumulator current. Since the rate of equalization of the concentration difference is proportional to i, but the rate of formation is proportional to the strength of the accumulator current I, and for a stationary condition the former must be equal to the latter, it follows that i^2 is

proportional to I^2. If C represents the proportionality factor, then the energy loss becomes

$$\varepsilon = C\frac{\gamma}{k} I^2 t \text{ volt-coulombs.}$$

This equation expresses the dependency of the energy loss upon the mechanical structure (porosity) of the plates (through γ), the conductivity of the acid within the plates, the current-strength, and the time.

Since the acid within the plates is more concentrated during charging and less concentrated during discharging than that without, we obtain a minimum for ε during charging by employing acid somewhat more dilute than that of maximum conductivity, while during discharge we obtain the same by using acid more concentrated. Therefore with approximately equal charge and discharge current-strength the accumulator operates with maximum working efficiency when the same is filled with acid of greatest conductivity i.e., 30.4 per cent H_2SO_4, density 1.224.

That is, the conductivity of the electrolyte is the determining factor for the working efficiency as well as the capacity. In fact the investigations of Heim show that the maximum working efficiency very nearly coincides with that of the capacity, as can be seen from the working efficiency curve of Fig. 19, p. 169. It is true the maximum lies at 22 per cent acid (measured in charged condition),

but this displacement of the maximum is very probably due to the longer interval between charge and discharge (see p. 170). According to the measurements of Earle as well as the investigations of Schenek the maximum working efficiency seems to lie quite accurately at 30 per cent acid (see Fig. 20).

This fact, that the conductivity of the acid is of such great influence upon the working capacity, also follows directly from the discussions on p. 171. It was there concluded that the lines of current can penetrate deeper in proportion to the conductivity of the acid.

Therefore when using acid of greatest conductivity the lines of current can spread themselves upon the maximum of surface, whereby the polarization becomes a minimum. The rapid rise of the working efficiency with the temperature and the falling off of the same upon the addition to the acid of poorly conducting substances, such as gelatinous silicic acid and the like, very easily find their explanation in the increase or decrease of the conductivity k.

For example, measurements made upon different types of accumulators showed that the conductivity of the accumulator acid is cut down to about one half by gelatinizing with silicic acid. According to our equation, then, the loss of energy in an accumulator with gelatinized acid ought to be twice as great as in one having pure acid. Measurements of Schoop, in his work entitled "Die Secondaerele-

mente," give as the difference between the charging and discharging work of an Oerlikon accumulator 51.04 watt-hours when using gelatinized acid, i.e., just about twice as great. Computing I^2t, we get 4134 in the former case and 4017 in the latter. According to the above equation, then, the energy loss of the accumulator with gelatinized acid must be $2 \cdot \frac{4017}{4134} = 1.95$ times greater than with pure acid, whereas the measurement gave 1.98.

In order to get an exact expression for the relation between energy loss and strength of the accumulator current, it would be necessary to introduce into the computation the shrinkage of the pores of the plates during passage of the current, similar to the method for getting the influence of current-strength upon capacity (p. 161). At present sufficiently accurate measurements are wanting in order to be able to test such an equation, so we refrain from deriving the same.

As a rough approximation for the purpose of a check calculation we can consider $\frac{r}{k}$ as independent of I and write the loss of work

$$\varepsilon = CI^2t (C = \text{const.}).$$

If we chose the constant C so as to include that loss of energy, likewise proportional to I^2t, due to Joule's heat, then the above equation gives the entire loss occurring in the accumulator, with the

exception of the very slight loss caused by self-discharge and gas evolution.

We can then with fair approximation consider the loss of work as proportional to the square of the current-strength; that is, it behaves as though caused by a large internal resistance. A test of this relation is contained in Table XVIII; the same gives measurements upon a Tudor and a Correns battery. The former were carried out by Berner, Conz, Peukert, and Voller, and the latter by Germershausen, Heim, W. Kohlrausch, and Seifert. Column 5 contains the values of C derived from the energy loss by means of the above equation. In the computation three measurements succeeding each other, in which I did not vary too much, were used. In the case of both batteries the values of C are as constant as can possibly be expected of that kind of a technical measurement, in spite of I^2 varying by as much as four times. The greater deviation of the second value of the Correns battery is undoubtedly to be attributed to some disturbance during the measurement, as the abnormally high working efficiency of 91 per cent also goes to show.

In order to give some idea as to how far such a constant permits the determination of the variation of the working efficiency with the strength of current, there are given in the last column of Table XVIII the working efficiencies for discharge, calculated from the mean values of C (for Tudor battery 0.0017, for Correns battery 0.00085) and

the work of charging, and alongside of these those measured.

TABLE XVIII.

	Duration in Hours.	Mean Current Strength, Amperes.	Watt-hours.	*C*	Working Efficiency of Discharge.		
					Measured.	Calculated.	
Charge....	5.4	134.3	1670				
Discharge .	4.5	152.7	1320	0.0019	0.76	0.79	Tudor battery.
Charge....	5.5	139.6	1800				
Charge....	4.37	175	1830				
Discharge .	3.45	195	1280	0.0017	0.75	0.75	
Charge....	3.83	179.3	1600				
Discharge .	2.0	311	1130				
Charge....	2.38	292	1720	0.0015	0.65	0.61	
Discharge .	2.0	302	1110				
Charge....	6.30	157	2170				
Discharge .	6.03	154.7	1850	0.0009	0.87	0.88	Correns battery.
Charge....	6.00	155	2060				
Charge....	4.78	178.8	1910				
Discharge .	4.60	196.7	1780	0.0005	0.91	0.86	
Charge....	4.90	183.4	1990				
Charge....	2.63	309	1570				
Discharge .	2.70	316.5	1950	0.0008	0.78	0.77	
Charge....	2.43	318.0	1500				

It is worth calling special attention to that it is the good metallic conducting property of lead sponge and peroxide that makes it possible for the lines of current to spread over a very large surface and therefore permits the taking of strong currents from the accumulator. In fact only such of the galvanic elements with solid, difficultly

soluble depolarizers can be used with strong currents, in which these depolarizers are metallic conducting bodies. For that reason the Cupron and Le Clanché elements, constructed respectively with conducting copper oxide and manganese dioxide, can be taxed with a much higher current density without polarizing than those elements (Clark calomel element) constructed with non-conducting mercury salts, even though mercurous sulphate and mercurous chloride are probably considerably more soluble than manganese dioxide and copper oxide. Hence in the construction of every technically serviceable element which contains solid, difficultly soluble active substances, it is essential that these substances possess metallic conductivity.

XIV.

CHANGES IN THE CELL DURING FORMATION.

THE behavior of the accumulator during charging and discharging, described in Chapter VIII, pertained to the same in condition for service. There are therefore still remaining to be treated the changes in the cell during formation. Here we must distinguish between the so-called Planté formation, in which the active mass is formed out of the lead carrier itself, and the formation after Faure, in which lead sponge and peroxide are formed from lead compounds placed upon the lead carriers. We shall first consider the latter mode of formation.

(*a*) *Formation of Faure Accumulators.*—As is well known, Faure plates are made by mixing lead oxide to a paste with dilute sulphuric acid (or possibly with solutions of sodium bisulphate or magnesium sulphate) and placing it upon leaden grids or corrugated leaden plates. In the course of several hours the sulphuric acid unites with the lead oxide to basic sulphate, whereby the mass

hardens (sets). The hardened paste consists then of a mixture of basic and neutral lead sulphate and unchanged lead oxide.

If, in place of litharge, red lead or a mixture of the two oxides was used, the paste contains lead peroxide in addition, which was formed according to the equation

$$Pb_3O_4 + 2H_2SO_4 = PbO_2 + 2PbSO_4 + 2H_2O.$$

In case of employing glycerine sulphuric acid, lead glycerate would also be found in the paste.

For the purpose of changing the lead sulphate into peroxide and lead sponge, the plates are introduced into a bath of dilute acid or a solution of acid sodium sulphate, bitter salts, or the like, and subjected to the action of the current.

We now want to try to find the most favorable conditions for this conversion, and, in particular, first for the lead-sponge electrode. Here we are concerned with separating the lead ions from the solution of sulphate which the paste gives. Experience has shown that the electrolytic reduction with stronger currents gives a large quantity of free hydrogen, i.e., a part of the current is employed without purpose for water electrolysis.

This fact is explained as follows: At the beginning of the electrolysis we have a saturated lead sulphate solution in close proximity to the conducting leaden carrier where the electrolysis takes place. As a result of the great over-voltage to which the evolution of hydrogen on lead is subject (see p. 17),

we at first have only a separation of lead and no hydrogen.

The potential prevailing at the electrode according to the osmotic theory is given by the expression (p. 49)

$$\varepsilon_p = \frac{RT}{2} ln \frac{C_p}{\left[\overset{++}{\mathrm{Pb}}\right]},$$

in which C_p is the solution pressure of lead sponge for lead ions and $\left[\overset{++}{\mathrm{Pb}}\right]$ the concentration of the lead ions in the sulphate solution. Electrolyzing with stronger currents, the lead ions in the vicinity of the conductor are electrolyzed out more rapidly than they can be replaced by diffusion from the sulphate mass, because the coarse-grained sulphate of the paste only slowly dissolves. The result is that the concentration of the lead ions decreases, and therefore the potential ε_p, according to the above equation, increases. This increasing of the cathodic potential will continue until ε_p has attained the value which is necessary for the separation of hydrogen on a lead surface.[1] From this moment on, along with lead ions, hydrogen ions will be liberated, and in addition to the above equation we have

$$\varepsilon'_p = RTln \frac{C_H}{\left[\overset{+}{\mathrm{H}}\right]},$$

[1] According to page 135 this potential measured against an hydrogen electrode is equal to 0.64 volt.

in which C_H is the solution pressure of hydrogen on a lead surface,[1] on which hydrogen is being evolved, and $\left[\overset{+}{\mathrm{H}}\right]$ the concentration of the hydrogen ions in the electrolyte.

Of course in case both lead and hydrogen are liberated $\varepsilon_p = \varepsilon'_p$. If we wish to effect that along with lead only a minimum of hydrogen is set free, we must see to it that ε'_p is greater than ε_p, i.e., we must seek to make the value of $\left[\overset{+}{\mathrm{H}}\right]$ as small and the value of $\left[\overset{++}{\mathrm{Pb}}\right]$ as great as possible. The first condition is easily fulfilled, by using as electrolyte, instead of dilute sulphuric acid, the solution of a neutral sulphate which contains very few $\overset{+}{\mathrm{H}}$ ions. As a matter of fact, experience has long since demonstrated that the formation proceeds more rapidly in neutral solution than in dilute acid. Suitable electrolytes are solutions of sulphates of sodium, potassium, magnesium, aluminium, and the like. The use of alkali sulphates is, however, less suitable, since electrolysis forms free alkali at the cathode, which converts the sulphate into hydroxide, which hydroxide in turn partly dissolves and so loosens up the paste. The employment of solutions of magnesium sulphate (bitter salt) or aluminium sulphate, whose electrolysis gives gelatinous hydroxides at the cathode, which are entirely

[1] This is in consequence of the retardation of the hydrogen evolution on a leaden surface (excess voltage 17) considerably greater than on a platinum surface.

harmless and neutralize the acid set free during formation, is much more satisfactory. The theory gives directly, as the most favorable electrolyte solutions, those which have long been recognized in actual practice as best serving the purpose.

The second possibility in the direction of accelerating the formation, that of increasing the concentration of the $[\overset{++}{Pb}]$ ions, cannot be realized in the presence of sulphates $(\overset{--}{SO_4}$ ions$)$. The removal of $\overset{++}{Pb}$ ions by the electrolysis can only be counteracted by increasing the solubility of the lead sulphate. This can easily be done by the addition of an ion which forms with lead ions a weakly dissociated salt.

An ion of this kind is, for example, the ion of acetic acid $(CH_3\overset{-}{C}O.O)$. Upon adding sodium acetate to a lead sulphate solution, the acetic ions continue to add $\overset{++}{Pb}$ ions, until the undissociated lead acetate formed is in dissociation equilibrium with the lead ions.

It is true by such an addition the solution is not enriched with lead ions, but rather to a considerable extent with lead salt, which constitutes a reservoir for lead ions, in that it replaces these by dissociation as soon as their concentration is diminished by electrolysis. Experiment shows that the formation is very much hastened by the addition of sodium acetate. All ions of weak acids forming a soluble lead salt act in a similar way. Unfortunately

there is this hindrance to its application in practice, namely, that the last traces of the substance added can only be removed with difficulty from the finished plate, and incomplete removal easily gives rise to etching of the lead and other disturbances.

We shall now turn our attention to the formation of the positive electrode. Here we are concerned with choosing conditions which are most favorable to the separation of the peroxide ions and at the same time keep the liberation of oxygen down to a minimum. It is most effective to increase as much as possible the extremely slight concentration of the $\overline{\overline{PbO_2}}$ ions. According to equation (11), p. 46, the concentration of the peroxide ions is given from that of the lead ions and hydrogen ions by

$$\left[\overline{\overline{PbO_2}}\right] = \text{const.} \frac{\left[\overset{++}{Pb}\right]}{\left[\overset{+}{H}\right]^4}.$$

In order to make the value of $\left[\overline{\overline{PbO_2}}\right]$ large, we must in this case also choose the acid concentration small, which means using a neutral solution of magnesium or aluminium sulphate. The influence of the acid concentration is much greater here than in the case of the separation of lead sponge, since the concentration of the peroxide ions increases inversely as the fourth power of the $\overset{+}{H}$ ions.

It goes without saying that the use of neutral solutions in the formation of Faure plates has

an object only when the acid liberated during formation is continually neutralized, which is best accomplished by suspended magnesium or aluminium hydroxide.

Of greater practical significance than the economical use of current are the structure and other properties of the lead sponge formed; as to this, however, we can at present obtain insight only by means of laborious experiments, for theoretical points of view are entirely lacking.

(*b*) *Planté Formation.*—We shall take up next the changes which take place on the electrode during the formation after Planté. As is well known, this mode of formation consists in converting the surface of bright lead plates, by electrolysis in dilute sulphuric acid, into peroxide on the one hand and into spongy lead on the other. Planté himself gave the following directions for his process: "On the first day allow the current of two bunsens to pass through the spiral in opposite directions from six to eight times; at the same time allow the time of charging to increase from a quarter of an hour to one hour. After each charging discharge the element. Finally, permit the element to stand until the next day, charged in a definite direction. Continue this operation on the same, continually increasing the duration of charging and the duration of standing." As soon as the element has reached, by such continued treatment, the maximum of capacity, then the charging current must not pass through the same

in different directions, but charging and discharging must always take place each in its own constant direction. Then the following applies: "There is in the beginning of the charging no evolution of gas; when this does set in, it is an indication that the charging is completed."

The necessity of a repeated reversal of the current direction is easily apparent, as the lead can be attacked and loosened up only when it is exposed to the action of the current as anode; therefore in case both electrodes are to be formed the direction of the current must be changed off and on. At first glance, however, the reason for the prescribed standing of the cell in the charged condition is not so evident.

This obscure action of rest is explained by the investigations of Gladstone and Tribe, who showed that during rest the peroxide, especially when the same is in thin layers, acts upon the underlying lead, by forming short-circuited small local elements, in which both lead and peroxide are changed into sulphate (equation 1). Thereupon a charging current finds a considerable quantity of sulphate and can form more peroxide than was possible at the previous charging. Discharging has a similar favorable effect upon the action of the current, in that through it the lead is freed from the protecting peroxide covering, thus offering fresh surfaces of lead to be acted upon. It is evidently for this reason that one electrolysis is not sufficient, because the lead at once is covered with a

protecting, conducting layer of peroxide, whereby the further action of the current is checked.

The only way to carry out the formation with a smaller amount of electrical energy and in a shorter time is to seek for means to prevent the separation of peroxide ions. This object can be attained in two ways: either by using a voltage so small that it is not sufficient to precipitate the peroxide ions from the electrolyte, or by adding to the acid electrolytes (salts or acids) whose anions can be separated out more readily (at a lower voltage) than the peroxide ion.

The first way is by guarding against the formation voltage being greater than 2 volts (i.e., greater than the E.M.F. of the accumulator for the particular density of acid).[1] The simplest and surest way of accomplishing this is by suspending the lead plate to be formed in dilute acid in short circuit with a charged positive accumulator electrode,

The energy set free at the accumulator electrode during the conversion of peroxide into sulphate is just insufficient, in view of the losses of potential always present, to reconvert sulphate into peroxide at the lead plate, so that lead is only changed into sulphate, which, since it is not a metallic conductor, cannot serve as a protection to the underlying lead; the formation takes place, however, in consequence of this arrangement, at the highest permissible voltage and current-strength.

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[1] D. R. P. No. 9166 of Ch. Pollak, Frankfort.

By warming the electrolyte to from 40° to 60° C., thereby providing for the most rapid diffusion of the acid through the sulphate layer, one can succeed in producing a sulphate layer equivalent to the quantity of current passing through the cell, which can be converted into peroxide or lead sponge by one charging with an increased voltage.

Formation takes place in this case, as I have convinced myself by experiments, exactly according to Faraday's law, and is therefore extremely reasonable; in addition this method has the advantage over those to be discussed presently in that the plates are not contaminated by any kind of detrimental substances. In this way sheet lead 0.3 mm. thick can be completely formed, through and through, in thirty-six hours.

The second way to effect an accelerated formation depends, as has been said, upon adding to the acid, anions which are separated out at a lower voltage than peroxide ions, and therefore prevent the precipitation of the latter.

All known methods of hastening Planté formation which depend upon additions to the acid are based upon this general principle. Such anions are naturally furnished by all substances which are capable of reducing lead peroxide, as acetic acid and acetates, tartaric acid and tartrates, oxalic acid, sulphurous acid and its salts, and the like.

Easily separated anions are given, for example, by all chlorides, nitrates, chlorates, perchlorates, and their respective acids.

All these substances, whose number might be considerably extended, have the effect of preventing the separation of peroxide, so that only sulphate is formed, which, as already mentioned, cannot check the progress of the formation.

In fact, through the substances named, a considerable acceleration of formation with more or less good results can be achieved. Unfortunately, however, these means have the serious drawback that the last traces of salt can be removed only with great difficulty from the finished plates, and slight quantities of salt left very considerably reduce the life of the plates.

The use of perchloric acid[1] or sulphurous acid seems to be least harmful, or possibly is entirely without any detrimental consequences.

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[1] D. R. P. No. 90446 of L. Locas in Hagen.

XV.

METHODS OF MEASUREMENT.[1]

THE best proof for theoretical conclusions is their numerical comparison with exact measurements. For that reason, in the investigations presented, especial emphasis has been placed upon confirmation by the results of measurements, and the latter have been given in detail. In order, however, not to disturb the theoretical continuity, the treatment of the methods of measurement were omitted; on account of the importance which they possess for scientific investigations upon accumulators, they will in conclusion be discussed connectedly.

The thorough testing of a storage-battery requires determinations of the E.M.F. and pole-potential, the capacity and working efficiency, as well as measurements of the internal resistance of the entire storage cell and the separate electrodes, under the most varied conditions of withdrawal

[1] As to detailed directions for carrying out electrical measurements the reader is referred to the classical work, Leitfaden der praktischen Physik, by F. Kohlrausch.

of current, temperature, concentration of the electrolyte, and the like.

(*a*) *Measurement of Electromotive Force and Pole-potential.*—The measurement of the E.M.F. and the pole-potential of a storage-battery is best accomplished by connecting with it a precision voltmeter, of the excellent quality furnished by the Weston Company, Siemens & Halske (Berlin), Hartmann & Braun (Frankfurt a. M.), Kaiser & Schmidt (Berlin). Since the accumulator polarizes when stronger currents are withdrawn and the loss of potential through the internal resistance can become appreciable, it is necessary for more accurate measurements to employ instruments with large resistance (over 100 ohms).

The accuracy of the measurements with such precision voltmetrs seldom exceeds several thousandths volt.

A somewhat greater accuracy (to within one-thousandth volt) is obtained with a Siemens torsion galvanometer, which, however, is less convenient and is subject to disturbance by outer magnetic influences. If a still greater accuracy is desired or if we have to examine a very small cell with a large internal resistance, the measurement can be made only with a calibrated mirror galvanometer or according to a compensation method. For this purpose any good mirror galvanometer is suitable. Those with fixed coil and movable magnet have the advantage of more exact deflections; those with fixed magnet and movable coil (galvanometer

after Deprez-d'Arsonval) have the good quality of being non-sensitive to external magnetic disturbances.

In series with the galvanometer are placed a commutator and a resistance of "Konstantan" wire, which latter is to be so regulated that 2 volts give a commutated deflection of about 250 mm. in the reading telescope. In the usual forms of the mirror galvanometer the resistance is from 10^4 to 10^5 ohms. To make the measurement, compare the deflection given by the E.M.F. to be determined with that of the known E.M.F. of a normal element (Clark or Weston cell). Indicating the E.M.F. of the normal element with E_n, that of the element to be measured with E_x, the galvanometer deflection with a_n and a_x respectively, then

$$E_x = E_n \frac{a_x}{a_n}.$$

This equation is based upon the assumption that the internal resistances of the elements are so small as to be negligible against the resistance of the external circuit—a condition that is always fulfilled with accumulators; with normal elements, however, it is very frequently not, because in these resistances of several thousand ohms and more easily arise, due to the formation of dense crystal crusts. In this case one can eliminate the influence of the internal resistance by not determining the deflection of the single elements, but by inserting both cells in the circuit at the same time, once

in series and once opposed to each other. If the deflection is a_2 when the cells are in series and a_1 when opposed, then

$$E_x = E_n \frac{a_2 + a_1}{a_2 - a_1}.$$

The most accurate and least faulty measurements of electromotive forces are those by Poggendorff's compensation method. Two small accumulators

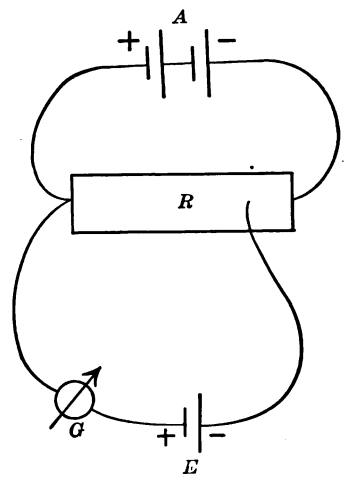

FIG. 22.

A, having a capacity of several ampere-hours, are connected through an ordinary resistance-box of 11000 ohms. The compensation circuit, which includes the element to be measured and a galvanometer or capillary electrometer as zero instru-

ment, is so arranged that one terminal is inserted back of the resistance 4000 ohms and the other at the opposite end of the resistance-box, as shown in Fig. 22. The measurement is made by drawing resistance-plugs until the deflection in the galvanometer disappears. If with the insertion of the normal element it requires a resistance of R_n ohms to produce zero deflection and R_x ohms with the insertion of the element to be measured, then

$$E_x = E_n \frac{R_x(4000+R_n)}{R_n(4000+R_x)}.$$

The compensation method has the advantage over the others that the element can be tested in an almost non-current flowing condition and the internal resistance is without influence. This method is to be looked upon as the most perfect of those mentioned, and is therefore at present almost exclusively employed in measurements of precision; most of the measurements contained in the previous chapters were made by means of it.

A good method to determine the E.M.F. of a cell while a current is flowing has not as yet been devised. The attempt has been made to make measurements by interrupting the accumulator current and at the same time connecting the cell with a delicate measuring instrument, with the aid of a key or vibrating tuning-fork or the like. The results obtained are, however, dependent upon the time which elapses between the opening of the circuit

and the adjustment of the instrument, so that they possess no significance. The only possibility of getting at the E.M.F. while a current is flowing is by determining by one of the subsequent methods the internal resistance with closed circuit, calculating from it the loss of potential (IR) in the cell and then by equations (48) and (49) (p. 106) the E.M.F.

The methods given permit the determination of the E.M.F. or pole-potential of the entire accumulator with any degree of accuracy; however, in a thorough testing of a storage-cell it is also necessary to measure the potential or variation in potential of each separate electrode. In order to do this we must introduce into the accumulator a third "auxiliary electrode" (measuring electrode) and determine the potential of the individual electrodes against it.

(*b*) *Measuring Electrodes.*—For less accurate measurements, as, for example, in determining the capacity of the separate electrodes of a storage-cell, an amalgamated zinc rod, about 10 cm. long and 1 cm. in diameter, constitutes a very suitable auxiliary electrode. The zinc rod is to be connected with one binding-post of the measuring instrument and dipped into the acid; the other binding-post of the instrument is to be attached to the electrode to be measured. In place of zinc one can take amalgamated cadmium, which is more slowly attacked by the acid and therefore gives somewhat more constant potentials. With acid of the usual density the voltage of zinc—lead

peroxide is about 2.41 volts, zinc—lead sponge about 0.40 volt, cadmium—lead peroxide about 2.17 volts, and cadmium—lead sponge about 0.16 volt.

The potential of the zinc and cadmium electrodes in dilute acid is certain only to within several hundredths volt, in consequence of the accidental and varying concentration of zinc and cadmium sulphate respectively, in immediate proximity to the electrode; for most technical measurements this accuracy is quite sufficient. The chief advantage of these auxiliary electrodes consists in the great ease with which they are made, their handiness, and the circumstance that through simple inspection one can at any time convince himself of their good condition. For precision measurements such electrodes are unsuitable on account of their inconstancy; for these, constant electrodes must be employed, i.e., electrodes which are reversible as regards one of the ions ($\overset{+}{H}$ or $\overset{--}{SO_4}$) contained in sulphuric acid.

Electrodes reversible as to $\overset{--}{SO_4}$ ions are given by all metals which form very difficultly soluble sulphates, for instance lead and mercury, while only the hydrogen electrode is reversible as to the second ion of sulphuric acid, the $\overset{+}{H}$ ion. It is simplest, therefore, in an accurate investigation to use a small, well-charged, positive or negative accumulator electrode, suspended in the cell in such a way that the fewest possible current lines strike it. Such accumulator electrodes are splendidly adapted

to potential measurements in sulphuric acid solutions. They are exceedingly constant and have the great advantage over the following ones that they will endure a relatively strong withdrawal of current and can therefore be used with a precision voltmeter.

The electrodes mentioned are excelled in constancy and reliability by the combination mercury—mercurous sulphate. It is, however, much more easily polarized and hence can only be used in galvanometric methods.

For measurements upon accumulators it is best to employ the same in the form of a dip electrode.

A glass vessel of the form given in Fig. 23 (one-third natural size), resembling a tobacco-pipe, has the widened portion filled to one third its height with purest mercury; placed upon the mercury we have a layer of about 1 cm. thickness, of purest mercurous sulphate, which had been stirred up to a thin paste with accumulator acid. The remaining space is entirely filled with acid.

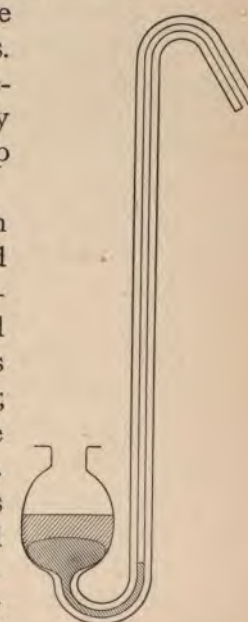

FIG. 23.

Connection is made with the mercury by means of a platinum wire passing through the capillary tube (1 mm. thread). The electrode can be suspended

directly in any accumulator. A detrimental contamination of the accumulator acid by mercury salts is not to be feared in view of the slight solubility of mercurous sulphate; and besides small quantities of mercury salts would not be injurious to the accumulator (see p. 136).

The potential difference of this electrode with acid of the usual density is about 1.05 volts against lead peroxide and 0.96 volt against lead sponge.

In conclusion there is to be mentioned a fifth kind of electrode, which is frequently employed to advantage in scientific investigations, on account of its simple theoretical treatment. It is the hydrogen electrode devised by Grove. This consists essentially of a well-platinized (coated with platinum-black) platinum-foil, dipped into dilute sulphuric acid, and over which bubbles of hydrogen are passing.

The electrode behaves as though it consisted of a metallic conducting modification of hydrogen, i.e., it is reversible with respect to hydrogen ions. A form suitable for accumulator measurements is shown in Fig 24, about one half natural size. Hydrogen, prepared from pure zinc and sulphuric acid, is conducted in through the tube r, and glides in bubbles over the cylindrical, platinized platinum-foil p, to escape through the narrowly drawn out tube r_2. The object of the cylindrical, hollow glass vessel v is to reduce the amount of acid to be saturated with gas to the smallest amount, and to bring the gas-bubbles

into intimate contact with the platinum-foil. It is also well to have the platinum-foil projecting somewhat into the gas space. Connection with the accumulator is brought about through the

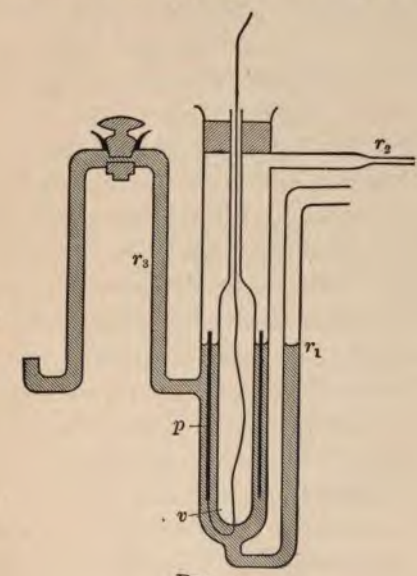

FIG. 24.

siphon r_3. The electrode assumes the correct potential, recognized by its constancy, after slowly bubbling hydrogen through it for about three hours. During this time the glass cock in the siphon is kept closed, so as to prevent a diffusion of hydrogen into the accumulator. It is opened only during the short time of the measurement. For the measurement with this electrode only the compensation method is to be used.

(*c*) *Measurement of Capacity and Working Efficiency.*—It is simplest to carry out the determination of both capacity and working efficiency at the same time. For this purpose the cell, discharged to its normal limit, i.e., until the potential has fallen off 10 per cent, is charged with a constant source of current (best a larger battery), having inserted a regulating resistance and an ammeter, and the pole-potential measured at short intervals. Any good precision voltmeter or torsion galvanometer is a suitable measuring instrument. To avoid errors through transition resistances, the same must be directly attached to the poles of the cell by means of special connectors. There is no object in adopting the more sensitive galvanometric methods for the measurement of voltage, except in the case of very small cells having a capacity of several ampere-minutes, because two capacity determinations on the same cell under apparently the same conditions never agree nearer than within 1 to 2 per cent. The results of the measurements are plotted on millimeter paper as shown in Fig. 7 (p. 108). When the voltage has reached the highest value (*D* in Fig. 7), the charging is interrupted and the cell is discharged in like manner through the adjustable resistance, until the pole-potential has fallen off by 10 per cent of its original value (*F* in Fig. 7).

The readings of the voltage at the beginning and end of the charging and discharging, where the pole-potential changes rapidly, must be made at

intervals of several minutes; during the linear course of the voltage, however, a few readings are sufficient.

If the cell has previously been strongly discharged or has stood unused for a long time, constant capacities are not obtained until the same has been charged and discharged a number of times.

Hence the safest way is to charge and discharge the cell several times with the particular current-strength before each capacity test.

The product of the duration of discharge measured in hours and the intensity of discharge gives the capacity of the cell; the ratio of the areas included, on the one hand, between discharge curve and coordinate axes, and, on the other hand, between charging curve and axes, gives the working efficiency (see pp. 153 and 175).

The areas can be determined either by means of a planimeter or by counting the square millimeters. To decide which of the two electrodes is responsible for a too small capacity or too small working efficiency, it is necessary to measure the voltage variation of the individual electrodes, during discharge, against an auxiliary electrode.

The most suitable auxiliary electrode in these measurements is either a small peroxide or lead-sponge electrode in open circuit. The defective electrode is recognized by the too early falling off of the voltage. Such determinations of the individual capacity of the negative and positive plates

should be made in every accumulator test. Determinations of capacity and working efficiency should always be accompanied by the temperature, acid density, and acid volume, since the results obtained are very greatly influenced by these magnitudes.

(*d*) *Measurement of the Internal Resistance.*—As is evident, the internal resistance of an accumulator in open circuit can in principle be measured by the same methods as that of any galvanic element; since, however, the resistance of even the smallest cells used amounts to only a few hundredths or thousandths ohm, the transition resistances at the binding-posts make themselves very much felt and cause most of the methods to give inaccurate results.

The only reliable method is the one of F. Kohlrausch, with alternating current and telephone, using at the same time the bridge arrangement of Matthiesen and Hockin, which makes it possible to eliminate the resistances at the connections. By adding the further modification of introducing a condenser into the arm of the bridge, in series with the telephone, we gain the advantage of requiring only two cells for the measurement, instead of three, and that the resistances of the individual cells can be individually determined. Fig. 25 shows the scheme of arrangement. *AB* represents a constantane[1] wire (measuring-wire), about 1 meter long and 1 to 2 mm. thick, stretched on a scale, on

[1] German Konstantan.

which is arranged a sliding contact K; I is a small inductorium [1] serving to furnish the alternating current, R_0 a known resistance of 0.01 to 0.1 ohm, and C a condenser of about 0.1 microfarad capacity. The cells to be measured are indicated by R_1 and R_2. To keep these from discharging themselves

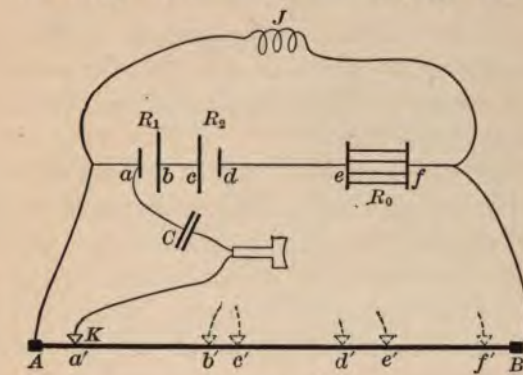

FIG. 25.

through the bridge, we must always use two, arranged to oppose each other, having equal electromotive forces (i.e., having acids of the same strength).

The measurement is made by first connecting the bridge to the cell at a by means of a special connector directly attached to the electrode, and thereupon moving the slide contact until we have a minimum of sound in the telephone, which is, say, at a'. Then the bridge is attached in a similar way at the points b, c, d, e, f, giving the slide con-

[1] The secondary coil as well as the telephone must be wound with 0.5 to 1 mm. diameter copper wire, since the bridge has a low resistance.

tact positions b', c', d', e', f'. The condenser keeps the cells from discharging themselves through the bridge. The points a, b, c, d, e, and f have relatively the same potential as a', b', c', d', e', and f'. Consequently the potential difference between these points is the same and the ratios of the resistances are $R_1 : R_0 = a'b' : e'f'$ and $R_2 : R_0 = c'd' : e'f'$, and are also as the corresponding lengths of the measuring-wire. That is, we get the resistances of the separate cells direct, expressed in units of the measuring resistance R_0.

This method enables one to measure resistances of cells in open circuit, from 0.001 ohm down, to within several per cent. It does not, however, allow the measurement to be made at the same time that the current is flowing. This is a decided drawback, because the variation of the resistance in consequence of the chemical changes in the cell is of special practical and theoretical interest. Suitable methods for such investigations have been devised by Boccali,[1] Uppenborn,[2] Froehlich,[3] Nernst and Haagn.[4]

Boccali, as shown in Fig. 26, uses the bridge arrangement of Mattheisen and Hockin for measuring the resistance during charging; R_1 indicates the accumulator, R_0 a known resistance of several

[1] Elektrotechn. Zeitschr. 1891, p. 51.

[2] *Ibid.*, p. 157.

[3] *Ibid.*, p. 370.

[4] Zeitschr. f. Elektrochem. III, p. 421, 1897, and Zeitschr. f. physik. Chem., Vol. XXIII, Heft I, 1897.

thousandths ohm, and AB a measuring-wire of constantane, 1 meter long and 0.5 mm. in diameter. M is the dynamo furnishing the charging current, and W an adjustable resistance. The charging current can be measured by the ammeter A. The regular fluctuations of the dynamo current, produced by the armature coils entering the magnetic

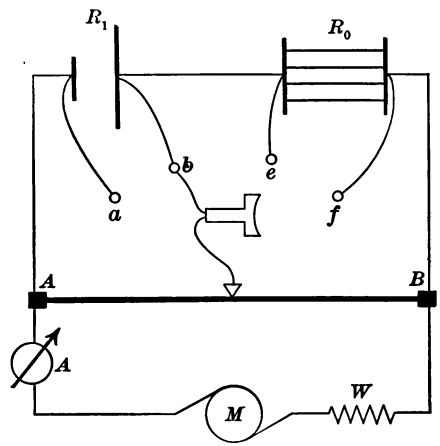

FIG. 26.

field, serve in place of the alternating current for making the measurements.

The telephone is successively attached at the points a, b, and f, and the resistance calculated from the positions of the sliding contact, as directed in the case of Fig. 25. If the test is to be made during discharge, the bridge wire is selected of such a strength that it can bear the current of the entire accumulator. In place of the dynamo M, an auto-

matic current-interrupter with series resistance is introduced. The fluctuations of the main current, produced by the interruptions in the shunt, are amply sufficient for the adjustment of the sound minimum. The resistance of the shunt must be considerably greater than that of the wire. To judge from the statements and measurements of Boccali, the method seems to give good results with resistances even as low as 0.001 ohm.

Uppenborn's method (l. c.) for determining the internal resistance of galvanic elements and accumulators in closed circuit is also a modification of Kohlrausch's bridge method. The measurement requires four (Fig. 27) as nearly as possible equal cells (R_1, R_2, R_3, R_4), which are arranged in series by twos and then the two groups connected opposing each other. In this way a potential difference between the points *c* and *d* is avoided and the cells cannot discharge themselves into the bridge.

Current can be conducted into or taken out of the cells at the points *ab* without in the least disturbing the resistance measurements. The remainder of the arrangement is in every respect like the ordinary telephone bridge and can be easily understood from the accompanying figure. The method undoubtedly gives good results with small cells in which the transition resistances at the connections play no part.

It is to be noted, however, that the resistance obtained is the mean value for the four elements, and that upon using stronger currents the individual

cells easily polarize differently, whereby potential differences arise between c and d, and the cells can partly discharge into the bridge.

The method [1] devised by Nernst and worked out by Haagn, in which condensers are introduced into the bridge arrangement, is free from these

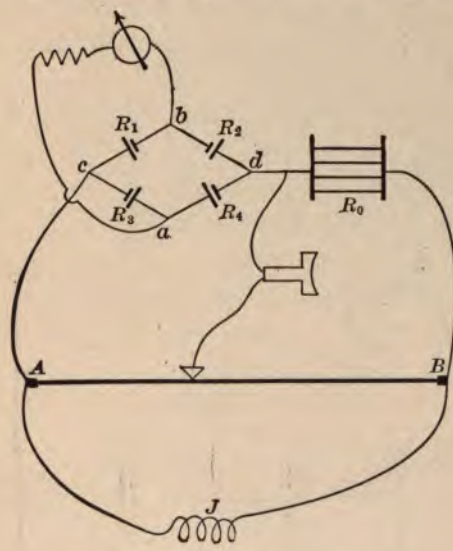

FIG. 27.

difficulties, and has to be regarded as the most perfect. As is well known, the ratio of the resistances in two arms of a bridge enables one to determine the ratio of two condensers inserted in the other two arms; conversely, if the ratio of the condensers is known, then that of the resistances can

[1] Zeitschr. f. physikal. Chem. 14, p. 623. 1894.

be calculated. By substituting condensers (C_1 and C_2) for the resistances of two arms of the bridge (see Fig. 28) we gain the advantage of being able to insert a single cell (R_1), for the reason that the condensers behave like an insulator toward the direct current, thereby preventing a discharge through the bridge. To keep a current from flowing through the inductorium (I), a condenser (C_3) is also introduced into this portion of the circuit.

The adjustment of the sound minimum is effected by varying the wire resistance in the fourth arm of the bridge (measuring-wire AB). As a wire it is most suitable to employ one of constantane,

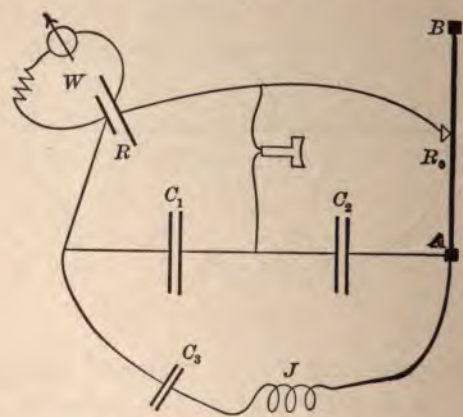

FIG. 28.

from 0.5 to 2 mm. in diameter, according to the resistance to be measured, stretched on a measuring rule, and having as a sliding contact a copper cup filled with mercury. The source of current most

to be recommended, on account of its silent action, is the wire-strand inductorium described by Nernst,[1] with a secondary winding of heavy wire; suitable capacities are condenser-boxes from 1 to 10 microfarads. The telephone coils must likewise be wound with heavy wire of low resistance. For the purpose of calibrating the entire apparatus thus set up, known wire resistances are substituted in the place of the cell and the corresponding positions on the variable resistance determined.

Thereupon in measuring open cells the resistances can be read off directly on AB; if, however, the cell is closed through a shunt (free from self-induction) of the resistance W, the resistance of the cell is given from the resistance R_0 read off, by

$$R_1 = \frac{R_0 \cdot W}{W - R_0}.$$

The greater the resistance of the shunt is, as compared with the internal resistance of the cell, the more exact the measurement. The described method gives good results down to several hundredths ohm, with cells in both open and closed circuit.

In the case of smaller resistances, the transition-resistance at the slide contact causes difficulty, and it is better to use Gahl's [2] arrangement, sketched in the accompanying figure. In this the resistance remains constant and only the bridge is moved;

[1] Zeitschr. f. physik. Chem. 14, p. 623. 1894.
[2] Zeitschr. f. Elektrochem. 7, Nr. 30 u. 31. 1901.

then the quality of the sliding contact has no influence upon the measurement. It is best to solder well all connections.

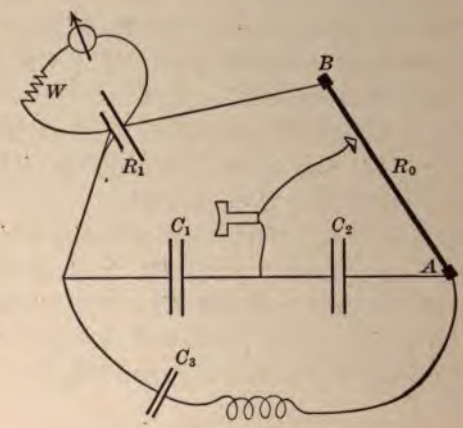

FIG. 29.

It is evident from what has been said that the measurement of the internal resistance of the accumulator is accompanied by difficulties, and therefore is only made in the case of scientific investigations. In practice it is quite sufficient, on account of its low value, to know the magnitude of the same. For this purpose it is accurate enough to calculate the resistance of the acid found between the plates, and to use from two to three times this value as the resistance of the cell.

To calculate the resistance of the acid, take the resistance of 1 c.c. of the acid employed, from the measurements of F. Kohlrausch given in Fig. 30, multiply this by the mean distance between

the plates measured in centimeters, and divide by the surface of the positive electrode expressed in square centimeters.

The calculation of the internal resistance of the accumulator, as recently proposed, from the heat developed while a current passes the same, is of

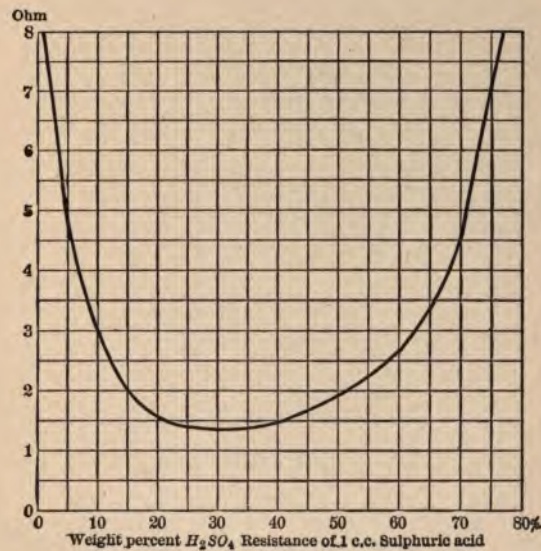

FIG. 30.

course entirely out of the question; for the greater part of the heat is not liberated according to Joule's law, but is set free by the equalization of the concentration differences developed at the electrodes. In addition to this, such a computation is also incorrect on account of the appreciable secondary heat of the accumulator (see pp. 33 and 34).

Also, the method still in use of getting at the internal resistance from the difference in potential between the cell in open and closed circuit is quite as full of error, because the polarization which sets in upon closing the circuit frequently exceeds the loss of potential through the internal resistance.

XVI.

Density and Percentage Strength of Mixtures of Sulphuric Acid and Water.

After Lunge and Isler.

Sp. Gr. at $\frac{15°}{4°}$ (Vacuum)	Degrees Beaumé.	Weight Per Cent H_2SO_4.	1 Liter contains Kg. H_2SO_4.	Sp. Gr. at $\frac{15°}{4°}$ (Vacuum)	Degrees Beaumé.	Weight Per Cent H_2SO_4.	1 Liter contains Kg. H_2SO_4.
1.000	0	0.09	0.001	1.160	19.8	22.19	0.257
1.005	0.7	0.83	0.008	1.165	20.3	22.83	0.266
1.010	1.4	1.57	0.016	1.170	20.9	23.47	0.275
1.015	2.1	2.30	0.023	1.175	21.4	24.12	0.283
1.020	2.7	3.03	0.031	1.180	22.0	24.76	0.292
1.025	3.4	3.76	0.039	1.185	22.5	25.40	0.301
1.030	4.1	4.49	0.046	1.190	23.0	26.04	0.310
1.035	4.7	5.23	0.054	1.195	23.5	26.68	0.319
1.040	5.4	5.96	0.062	1.200	24.0	27.32	0.328
1.045	6.0	6.67	0.071	1.205	24.5	27.95	0.337
1.050	6.7	7.37	0.077	1.210	25.0	28.58	0.346
1.055	7.4	8.07	0.085	1.215	25.5	29.21	0.355
1.060	8.0	8.77	0.093	1.220	26.0	29.84	0.364
1.065	8.7	9.47	0.102	1.225	26.4	30.48	0.373
1.070	9.4	10.19	0.109	1.230	26.9	31.11	0.382
1.075	10.0	10.90	0.117	1.235	27.4	31.70	0.391
1.080	10.6	11.60	0.125	1.240	27.9	32.28	0.400
1.085	11.2	12.30	0.133	1.245	28.4	32.86	0.409
1.090	11.9	12.99	0.142	1.250	28.8	33.43	0.418
1.095	12.4	13.67	0.150	1.255	29.3	34.00	0.426
1.100	13.0	14.35	0.158	1.260	29.7	34.57	0.435
1.105	13.6	15.03	0.166	1.265	30.2	35.14	0.444
1.110	14.2	15.71	0.175	1.270	30.6	35.71	0.454
1.115	14.9	16.36	0.183	1.275	31.1	36.29	0.462
1.120	15.4	17.01	0.191	1.280	31.5	36.87	0.472
1.125	16.0	17.66	0.199	1.285	32.0	37.45	0.481
1.130	16.5	18.31	0.207	1.290	32.4	38.03	0.490
1.135	17.1	18.96	0.215	1.295	32.8	38.61	0.500
1.140	17.7	19.61	0.223	1.300	33.3	39.19	0.510
1.145	18.3	20.26	0.231	1.305	33.7	39.77	0.519
1.150	18.8	20.91	0.239	1.310	34.2	40.35	0.529
1.155	19.3	21.55	0.248	1.315	34.6	40.93	0.538

DENSITY AND PERCENTAGE STRENGTH OF MIXTURES OF SULPHURIC ACID AND WATER.—*Continued.*

Sp. Gr. at $\frac{15°}{4°}$ (Vacuum)	Degrees Beaumé.	Weight Per Cent H_2SO_4.	1 Liter contains Kg. H_2SO_4.	Sp. Gr. at $\frac{15°}{4°}$ (Vacuum)	Degrees Beaumé.	Weight Per Cent H_2SO_4.	1 Liter contains Kg. H_2SO_4.
1.320	35.0	41.50	0.548	1.525	49.7	62.06	0.946
1.325	35.4	42.08	0.557	1.530	50.0	62.53	0.957
1.330	35.8	42.66	0.567	1.535	50.3	63.00	0.967
1.335	36.2	43.20	0.577	1.540	50.6	63.43	0.977
1.340	36.6	43.74	0.586	1.545	50.9	63.85	0.987
1.345	37.0	44.28	0.596	1.550	51.2	64.26	0.996
1.350	37.4	44.82	0.605	1.555	51.5	64.67	1.006
1.355	37.8	45.35	0.614	1.560	51.8	65.08	1.015
1.360	38.2	45.88	0.624	1.565	52.1	65.49	1.025
1.365	38.6	46.41	0.633	1.570	52.4	65.90	1.035
1.370	39.0	46.94	0.643	1.575	52.7	66.30	1.044
1.375	39.4	47.47	0.653	1.580	53.0	66.71	1.054
1.380	39.8	48.00	0.662	1.585	53.3	67.13	1.064
1.385	40.1	48.53	0.672	1.590	53.6	67.59	1.075
1.390	40.5	49.06	0.682	1.595	53.9	68.05	1.085
1.395	40.8	49.59	0.692	1.600	54.1	68.51	1.096
1.400	41.2	50.11	0.702	1.605	54.4	68.97	1.107
1.405	41.6	50.63	0.711	1.610	54.7	69.43	1.118
1.410	42.0	51.15	0.721	1.615	55.0	69.89	1.128
1.415	42.3	51.66	0.730	1.620	55.2	70.32	1.139
1.420	42.7	52.15	0.740	1.625	55.5	70.74	1.150
1.425	43.1	52.63	0.750	1.630	55.8	71.16	1.160
1.430	43.4	53.11	0.759	1.635	56.0	71.57	1.170
1.435	43.8	53.59	0.769	1.640	56.3	71.99	1.181
1.440	44.1	54.07	0.779	1.645	56.6	72.40	1.192
1.445	44.4	54.55	0.789	1.650	56.9	72.82	1.202
1.450	44.8	55.03	0.798	1.655	57.1	73.23	1.212
1.455	45.1	55.50	0.808	1.660	57.4	73.64	1.222
1.460	45.4	55.97	0.817	1.665	57.7	74.07	1.233
1.465	45.8	56.43	0.827	1.670	57.9	74.51	1.244
1.470	46.1	56.90	0.837	1.675	58.2	74.97	1.256
1.475	46.4	57.37	0.846	1.680	58.4	75.42	1.267
1.480	46.8	57.83	0.856	1.685	58.7	75.86	1.278
1.485	47.1	58.28	0.865	1.690	58.9	76.30	1.289
1.490	47.4	58.74	0.876	1.695	59.2	76.73	1.301
1.495	47.8	59.22	0.885	1.700	59.5	77.17	1.312
1.500	48.1	59.70	0.896	1.705	59.7	77.60	1.323
1.505	48.4	60.18	0.906	1.710	60.0	78.04	1.334
1.510	48.7	60.65	0.916	1.715	60.2	78.48	1.346
1.515	49.0	61.12	0.926	1.720	60.4	78.92	1.357
1.520	49.4	61.59	0.936	1.725	60.6	79.36	1.369

DENSITY AND PERCENTAGE STRENGTH OF MIXTURES OF SULPHURIC ACID AND WATER.—*Continued.*

Sp. Gr. at $\frac{15°}{4°}$ (Vacuum)	Degrees Beaumé.	Weight Per Cent H_2SO_4.	1 Liter contains Kg. H_2SO_4.	Sp. Gr. at $\frac{15°}{4°}$ (Vacuum)	Degrees Beaumé.	Weight Per Cent H_2SO_4.	1 Liter contains Kg. H_2SO_4.
1.730	60.9	79.80	1.381	1.826	65.3	91.25	1.666
1.735	61.1	80.24	1.392	1.827	—	91.50	1.671
1.740	61.4	80.68	1.404	1.828	65.4	91.70	1.676
1.745	61.6	81.12	1.416	1.829	—	91.90	1.681
1.750	61.8	81.56	1.427	1.830	—	92.10	1.685
1.755	62.1	82.00	1.439	1.831	65.5	92.30	1.690
1.760	62.3	82.44	1.451	1.832	—	92.52	1.695
1.765	62.5	82.88	1.463	1.833	65.6	92.75	1.700
1.770	62.8	83.32	1.475	1.834	—	93.05	1.706
1.775	63.0	83.90	1.489	1.835	65.7	93.43	1.713
1.780	63.2	84.50	1.504	1.836	—	93.80	1.722
1.785	63.5	85.10	1.519	1.837	—	94.20	1.730
1.790	63.7	85.70	1.534	1.838	65.8	94.60	1.739
1.795	64.0	86.30	1.549	1.839	—	95.00	1.748
1.800	64.2	86.90	1.564	1.840	65.9	95.60	1.759
1.805	64.4	87.60	1.581	1.8405	—	95.95	1.765
1.810	64.6	88.30	1.598	1.8410	—	97.00	1.786
1.815	64.8	89.05	1.621	1.8415	—	97.70	1.799
1.820	65.0	90.05	1.639	1.8410	—	98.20	1.808
1.821	—	90.20	1.643	1.8405	—	98.70	1.816
1.822	65.1	90.40	1.647	1.8400	—	99.20	1.825
1.823	—	90.60	1.651	1.8395	—	99.45	1.830
1.824	65.2	90.80	1.656	1.8390	—	99.70	1.834
1.825	—	91.00	1.661	1.8385	—	99.95	1.838

INDEX.

PAGE

Accumulator, acid coefficient of..... 66
as apparatus for determining the change in free energy produced by mixing sulphuric acid solutions..... 64
application of *Nernst's* osmotic theory to concentration chains of..... 89
concentration chains, measurements of, *Mugdan*..... 91
electrode potentials, dilution coefficients of..... 88
electrodes in combination with mercurous sulphate electrode... 79
electrodes, potentials against hydrogen electrodes..... 79
latent contents of..... 165
paste..... 185, 186
recovery of..... 129
temperature coefficient of..... 93
Acid coefficient of the accumulator..... 65
Acid concentration, calculation of the E.M.F. from..... 66
Acid-density, effect upon sulphatization 143
for maximum capacity..... 170, 171
influence upon capacity..... 168
influence upon loss of energy..... 177
influence upon rate of self-discharge of lead-sponge electrode.. 139
Acid, sulphuric, table of densities, etc..... 219
Active mass, analysis of..... 7
peroxide in..... 6
Aluminium sulphate, as formation electrolyte..... 188, 190
Aron, measurement of consumed sulphuric acid 8
Auxiliary electrode..... 201
Ayrton, analytical investigations of active mass 6, 7

PAGE
Behavior of the accumulator during charging and discharging..... 106
Berner, test of energy-loss equation..... 182
Berthelot, persulphuric acid by electrolysis..... 18
Bitter salts..... 186
Boccali, method of measuring internal resistance in closed circuit.....210, 211
observations upon resistance during charge and discharge..... 149

Cadmium, amalgamated, as auxiliary electrode..... 201
electrode, voltage against lead peroxide..... 202
voltage against lead-sponge..... 202
Calculation of size of element for a given taxation..... 167
Capacities, calculated and found..... 159
Capacity areas, measuring of..... 207
curve, theory of..... 161
curve, with variable current, theory of..... 164
determined by the conductivity of the electrolyte..... 172
equation, for a wider range, *Liebenow*..... 158
equation, for rapid discharge, *Schroeder*..... 157
equation, for slow discharge, *Liebenow*..... 157
equation of *Peukert*..... 159
factor *n*, for various accumulator systems..... 160
individual, positive and negative plates, measurement of..... 207
influence of acid density upon..... 168
influence of current strength upon..... 155
influence of temperature upon..... 172
influence of thickness of plate upon..... 168
maximum..... 170
maximum, theory of..... 171
measurement of..... 206
of the accumulator..... 153
relation to *Faraday's* law..... 153
relation to time of discharge, *Peukert*..... 159
relative, of lead-sponge and peroxide electrode..... 155
Caspari, experiments upon evolution of hydrogen on metals..... 16
see *Nernst*..... 135
Cell, changes in, during formation..... 185
Change in volume during charging and discharging..... 103
in volume during discharge, by direct measurement..... 104

PAGE
Changes in the cell during formation 185
in the open cell 129
on the electrode in *Planté* formation 191
Charge, variation of resistance during 149
Charging and discharging voltage, difference between, with varying current strength 121
Charging curve, discussion of 112
Chemical equation for current-producing action 3
Chemical equations for theory of *Le Blanc* 40
equilibrium and E.M.F. of the accumulator 70
theory of origin of current 1
Compensation method of *Poggendorff* 199
Concentration at electrodes, influence upon internal resistance 151
chains of accumulator, measurements by *Mugdan* 91
changes produced by electrolytic migration 123
of acid, influence upon capacity 168
of tetravalent lead ions 48
polarization, effect upon working efficiency 176
Condensers, use of, in measuring internal resistance 208, 209
Conditions most efficient for *Planté* formation 194
most favorable for *Faure* formation 186
most favorable for separation of peroxide ions 190
Conductivity of sulphuric acid, temperature coefficient of 172
of the electrolyte, relation to capacity 172
of the electrolyte the determining factor in working efficiency .. 179
Constant electrode, mercury—mercurous sulphate 203
electrodes 202
electrodes, charged accumulator plates as 202
Constantane wire 198
Contact, slide, mercury 214
Contents, latent, of the accumulator 165
Conz, test of energy-loss equation 182
Current density, effect upon accumulator 14
Current-strength, effect upon resistance 148
influence upon capacity 155
influence upon loss of energy 177, 181, 182
" " " " " , measurements 183
Currents, strong, depolarizers 183
Curve, capacity, theory of 161

PAGE
Curves, E.M.F. during charge and discharge 108
influence of temperature upon capacity 173
Dangerous metals, to the accumulator 135
Darrieus, theory of origin of current 18
Decomposition of lead peroxide 5
Degree of efficiency 174
dependent upon purity of the materials 175
Density and percentage strength of mixtures of sulphuric acid and water 219
Density of acid, influence upon capacity 168
Depolarizers, difficultly soluble and metallic conducting 184
Determining internal resistance of accumulator, method of *Nernst*. 148
Dieterici, vapor pressure of sulphuric acid solutions 61, 62
Diffusion law of *Fick* 130
Dilute sulphuric acid, dissociation of 66
Dilution coefficients 77
of the accumulator electrode potentials 88
Dilution of acid, effect upon electrode potential 125
Dip electrode 203
Discharge, intensity of, effect upon capacity 156
variation of resistance during 149
Discharging curve, discussion of 115
Dissociation of dilute sulphuric acid 66
Distillation, work of 59
Dolezalek, see *Nernst* 113
Duncan, absorption and liberation of heat during discharging and charging 32
Earle, influence of acid concentration upon capacity, measurement of 169, 170
Efficiency, degree of 174
working 174
working, determining factor of 179
working, effect of concentration polarization upon 176
working, effect of temperature upon 180
working, effect upon, of poorly conducting additions to the electrolyte (gelatinization of the acid) 180
working, maximum 179
working, measurement of 206

PAGE
Efficiency, working, ratio of surfaces 176
Elbs and *Schoenherr*, formation of persulphuric acid 19
Elbs, electrolytic lead tetracetate 42
explanation of sulphatization 141
theory of origin of current 21
Electrical energy, laws of transformation 25
Electrode, auxiliary 201
changes on, during *Planté* formation 191
constant, mercury—mercurous sulphate 203
hydrogen, *Grove* 204, 205
negative, formation of 186
positive, formation of 190
potential, effect of dilution of acid upon 125
Electrodes, accumulator, as constant electrodes 202, 208
constant 202
influence upon resistance of concentration at 151
lead-sponge and peroxide, relative capacity of 155
measuring 201
reversible as to hydrogen ions 202
reversible as to $\overline{SO}_4$ ions 202
Electrolysis of dilute sulphuric acid between platinum, and lead electrodes 14, 15
Electrolyte, neutral sulphate 188
Electrolytes, formation 188
Electrolytic solution tension 36
E.M.F., a linear function of the temperature 99, 100
and acid concentration, experimental proof of 70
and chemical equilibrium, van't Hoff's equation for 70
and heat effect 26
increase of, by reduction of vapor pressure of the acid 63
influence of external pressure upon 101
maximum temperature influence upon 97
measurements of concentration chains involving lead, lead peroxide, lead sulphate, and sulphuric acid 85
measurements of mercury against lead and lead peroxide respectively 80
methods of measurement 197
of accumulator, change with acid density 12
of accumulator, equation for, below 0.0005 normal acid 71

PAGE
E.M.F. of accumulator from thermochemical data..... 30
of accumulator with dilute sodium hydroxide solution..... 73
of accumulator with pure lead sulphate..... 72
of charged positive plate against zinc..... 5
of lead accumulator at 0° C., calculated and found..... 62
of the accumulator, equation for..... 50
of the accumulator from the concentration of the acid..... 66
of the accumulator, sodium hydroxide saturated with lead hydroxide..... 50
of the accumulator, parts due to reduction of peroxide, oxidation of lead sponge, change of oxide into sulphate, and sulphuric acid concentration chain..... 74
of *Weston* normal element..... 66
temperature coefficient of..... 26
variation with acid concentration..... 52
variation with acid density, thermodynamical calculation of... 55
with current flowing, measurement of..... 201
with variation of acid density..... 55
v. Ende, solubility of lead chloride in hydrochloric acid..... 143
Energy, chemical, transformation of..... 25
loss of, attributable to each of the two electrodes..... 128
loss of, equations.....179, 181
loss of, equations, test of..... 183
loss of, influence of acid density upon..... 177
loss of, influence of current strength upon.....177, 181, 182
loss of, influence of current strength upon, measurements..... 183
loss of, in the accumulator..... 108
Equation for current producing chemical action..... 3
for E.M.F. of the accumulator..... 50
for influence of thickness of plate upon capacity, *Liebenow*.... 168
for rapid-discharge capacity, *Schroeder*..... 157
for slow-discharge capacity, *Liebenow*..... 157
for the E.M.F. from the concentration of the acid..... 66
fundamental..... 3
of *v. Helmholtz*..... 26
of *Peukert*, for capacity..... 159, 160
Equations, chemical, for theory of *Le Blanc*..... 40
degree of efficiency.....174, 175
energy loss.....179, 181

PAGE
Equations, energy loss, test of. 183
working efficiency. 176
Evolution of hydrogen on metals, theory of. 15
Excess voltage 113
Experiment showing variations in concentration at accumulator electrodes 112

Factor *n*, of capacity 159, 160
Farad. 37
Faraday's law, in relation to capacity 153
Faure formation. 185
Fick, diffusion law of 129
diffusion law of, applied to relation between capacity and current strength. 161
Foerster, electrolytic lead tetrachloride from lead chloride 42
Formation and decomposition of lead peroxide and lead. 5
Formation and decomposition of lead sulphate and sulphuric acid. . 7
Formation, changes in cell during 185
electrolytes. 188
Faure, most favorable conditions. 186
ions during. 188, 189
negative plate. 186
of *Faure* 185
of *Planté*. 185, 191
of positive electrodes. 190
Formula of *Nernst*, applied to theory of *Liebenow* 49
Frankland, other sulphuric acid compounds. 7, 8
Fresenius, solubility of lead sulphate. 47, 72
Friedrich, tetrachloride of lead. 41
Froehlich, internal resistance in closed circuit. 210

Gahl, modified arrangement of *Nernst* and *Haagn* 215
Galvanic combinations of accumulator electrodes with hydrogen electrodes 76
with mercurous sulphate electrodes 79
Galvanic element, latent heat of. 32
Galvanometers. 197, 198
Gas evolution, retardation of. 17
Germershausen, test of energy loss equation. 182
Gilbaut, effect of pressure upon E.M.F. of various galvanic elements 104

PAGE

Gladstone, analysis of active mass..... 7
study of compounds of *Frankland*..... 7
Gladstone and *Hibbert*, E.M.F. at different acid concentrations 54
study of concentration chains involving lead, lead peroxide, lead sulphate, and sulphuric acid..... 82
Gladstone and *Tribe*, chemical theory of secondary batteries 2
dark coating on negative electrode observed by..... 117
object of rest during *Planté* formation..... 192
spontaneous discharge due to local action..... 137
sulphate theory 2
Glycerine, in accumulator paste..... 186
Grove, hydrogen electrode.....204, 205

Haagn, distribution of the variations in resistance in relation to the electrodes 152
effect of current strength upon resistance..... 148
resistance with slow and rapid discharge 151
see *Nernst*.....210, 213
study of internal resistance of the accumulator..... 148
Haeberlein, measurements of resistance during discharge of the accumulator..... 109
observations on resistance during charge and discharge..... 149
Hallwachs, measurements of resistance during charge and discharge 150
Hastening of *Planté* formation..... 194
Heat effect of accumulator reaction..... 29
Joule..... 33
latent, of galvanic element..... 32
loss in cell..... 177
of dilution of sulphuric acid..... 57
of formation of lead peroxide..... 29
of reaction of lead peroxide, lead, and sulphuric acid..... 28
secondary, of accumulator..... 33
Heim, increase of sulphatization with acid density 143
influence of acid concentration upon E.M.F..... 52
influence of acid density upon capacity, measurement of..... 169
see *Kohlrausch*..... 8
test of energy-loss equation 182
v. Helmholtz, equation of..... 26
"free energy".....25, 26

PAGE

v. Helmholtz, method of calculating E.M.F. of calomel cell as dependent on concentration of its solution 57
Heydweiler, see *Kohlrausch*..... 46
Hibbert, see *Gladstone*.....7, 55, 82
Hittorf, migration number of sulphuric acid.....84, 88
Hockin, see *Matthiesen*..... 208
van't Hoff's equation for the relation between E.M.F. and chemical equilibrium..... 70
Hydrochloric acid, effect on solubility of lead chloride..... 143
Hydrogen, cause of self-discharge..... 139
electrode, galvanic combinations with accumulator electrodes 76
electrode, *Grove*.....204, 205
ions, influence on concentration of peroxide ions..... 190
ions, reduction of concentration during formation..... 188
liberation during formation 186
minimum liberation during formation, conditions for..... 188
occlusion by lead..... 17
theory of evolution on metals..... 15
Hydrolytic dissociation of lead sulphate.....72, 73

Impurities, oxidizable, spontaneous discharge caused by..... 138
Inductorium, wire strand, *Nernst*..... 215
Influence of acid density upon capacity..... 168
of external pressure upon E.M.F..... 101
of temperature upon capacity..... 172
of thickness of plate upon capacity, equation for..... 168
Internal resistance, approximate, from resistance of the acid....216, 217
calculation from heat developed 217
from difference in potential of cell in open and closed circuit... 218
measurement in open and closed circuit (*Nernst* and *Haagn*) modified by *Gahl*..... 216
measurement of..... 208
Nernst's method of determining..... 148
of the accumulator 147
Ions, bivalent lead, effect on E.M.F..... 50
favorable to *Planté* formation..... 194
hydrogen, decrease of, during formation..... 188
lead..... 48
lead, increase of, during formation..... 189

PAGE
Ions, lead peroxide....43, 48
lead peroxide, effect on E.M.F.... 50
tetravalent lead 42
Irreversibility, distribution of, between the two electrodes.... 122
Isler, see *Lunge*.... 219

Joule heat.... 33

Kayser and *Ost*, see *Kugel*.... 136
v. Knorre, self-discharge by manganese salts.... 138
Kohlrausch and *Heydweiler*, first step of water ionization 46
Kohlrausch and *Rose*, solubility of lead hydroxide in pure water... 47
solubility of lead sulphate in water....47, 72
Kohlrausch, measurement of consumed sulphuric acid.... 8
Kohlrausch F., method of measuring internal resistance.... 208
Kohlrausch, temperature coefficient of conductivity of sulphuric acid 172
Kohlrausch W., test of energy-loss equation.... 182
Kugel, spontaneous discharge by metallic impurities.... 136

Lamb, see *Ayrton*.... 6, 7
Latent contents of the accumulator.... 165
heat of galvanic element.... 32
Lead, bivalent ions, effect on E.M.F. of concentration of.... 50
chloride, hydrolysis of 73
chloride, solubility of, in hydrochloric acid.... 143
disulphate.... 23
hydroxide, solubility in pure water.... 47
ions, increase of, during formation.... 189
oxides, E.M.F. against zinc.... 5
oxide, paste 185
peroxide, heat of formation of.... 29
peroxide, hydrated 5
peroxide ions by hydrolysis.... 43
peroxide ions, concentration of, in sulphuric acid containing lead sulphate 48
peroxide ions, effect on E.M.F. of concentration of.... 50
salts, other than lead sulphate 7
sulphate, basic.... 186
sulphate, formation and decomposition of.... 7
sulphate, hydrolytic dissociation of.... 72

PAGE
Lead sulphate, increase of solubility 189
sulphate, neutral 186
sulphate, solubility of 71, 72
sulphate, solubility of, in sulphuric acid 144
sulphate, solubility of, in water 47
tetracetate 42
tetrachloride 41
tetravalent 22
tetravalent ions 42
tetravalent ions, concentration of 48
Le Blanc, application of ion theory to the accumulator 39
theory of 39
theory of, difference from theory of *Elbs* 41
Ley, hydrolysis of lead chloride 73
Liebenow, application of *Nernst's* formula to theory of 49
equation for influence of thickness of plate upon capacity 168
equation for slow-discharge capacity 157
experiment to demonstrate acid shortage in discharging with stronger currents 154
proof of existence of lead peroxide ions 44
theory of 42
theory of capacity curve with variable current 164
Liebenow's peroxide-ion theory, application of, in calculating the E.M.F. 67
Litharge, paste 186
Local action, spontaneous discharge of positive plate by 137
Loomis, dissociation of dilute sulphuric acid 66
Loppe, test of *Peukert's* equation 160
Loss, heat 177
of energy, equations 179, 181
of energy in the accumulator, explanation of 110
of energy, test of equations 183
Lunge and *Isler*, table of densities, etc., of sulphuric acid and water 219

Magnesium sulphate 185
as formation electrolyte 188, 190
Manganese salts, cause of self-discharge 138
Mass action, law of, applied to the chemical equation of the action in the accumulator 69

PAGE
Matthiesen and *Hockin*, bridge arrangement of.....208, 210
Maximum capacity, *Earle*..... 170
Heim..... 170
theory of..... 171
Maximum working efficiency, measurements by *Heim*, *Earle*, *Schenek*.....179, 180
Measurement, methods of..... 196
of capacity and working efficiency..... 206
of E.M.F..... 197
of internal resistance..... 208
of pole-potential..... 197
Measuring-electrodes..... 201
Mercurous sulphate electrode in combination with accumulator electrodes..... 79
Mercury in the accumulator..... 136
Mercury—mercurous sulphate electrode..... 203
Mercury, potential difference against lead peroxide..... 204
potential difference against lead-sponge..... 204
slide contact..... 214
Metallic conducting depolarizers..... 184
Metals dangerous to the accumulator..... 135
Methods of measurement..... 196
Meyer, investigation of temperature coefficient of *Planté* element... 93
Migration, calculation of, by *Nernst*..... 123
number of sulphuric acid..... 84
numbers of sulphuric acid, *Stark*..... 91
Minimum of sulphatization..... 145
Mixtures, sulphuric acid and water, densities of..... 219
Moore, study of rate of recovery..... 131
Mugdan, effect of persulphuric acid on E.M.F..... 20
electrolytic migration of the acid..... 123
measurements of E.M.F. of accumulator concentration chains.. 91
on formation of sulphate..... 11
polarization of the separate electrodes.....126, 127
study of concentration chains involving lead, lead peroxide, lead sulphate, and sulphuric acid..... 82

Negative plate, formation of..... 186
Nernst, agreement between change of free energy and heat effect on mixing sulphuric acid solutions..... 63

PAGE

Nernst and *Caspari*, non-reversibility of liberation of hydrogen on metals 135
and *Dolezalek*, explanation of excess voltage 113
and *Haagn*, internal resistance in closed circuit, method of measurement.....210, 213, 214
electromotive activity of small concentration of lead peroxide ions 48
equation of..... 38
method of determining internal resistance of accumulator 148
migration calculation 123
non-reversibility of decomposition of lead disulphate..... 22
osmotic theory of galvanic cell 36
potential difference of metal against solution..... 134
theory of evolution of hydrogen on metals..... 15
wire-strand inductorium 215
Nernst's formula applied according to *Liebenow's* theory..... 49
osmotic theory, applied to the concentration chains of the accumulator..... 89
Neutral sulphate, formation electrolyte..... 188
Nickel, cobalt, iron, conditions of precipitation by lead..... 134
"Nutzeffekt"..... 175

Open cell, changes in..... 129
Origin of current, theory of *Darrieus*..... 18
theory of *Elbs* 21
Osmotic theory, applied to concentration chains of the accumulator 89
of galvanic cell..... 36
of origin of current..... 36
Oxide of lead, paste..... 185
Oxygen, cause of self-discharge..... 138

Paste, accumulator.....185, 186
Perchloric acid, use in *Planté* formation..... 195
Peroxide electrode, action of, according to *Liebenow*..... 42
Peroxide ions, concentration of.....46, 190
conditions most favorable to separation of..... 190
prevention of separation of..... 193
Persulphuric acid, formation of.....18, 19
Peukert, relation of capacity to time of discharge..... 159

PAGE
Peukert, test of energy-loss equation 182
Planimeter, for determining capacity areas 207
Planté, directions for formation of plates..... 191
formation, hastening of..... 194
formation, most efficient conditions for 194
formation of.....185, 191
formation, rest during..... 192
theory of..... 1
Plate thickness, influence upon capacity..... 168
Plates, E.M.F. against hydrogen electrode 13
see Electrodes.
Platinum, amount causing rapid self-discharge of negative plate... 136
Poggendorff's compensation method..... 199
Polarization, concentration, effect upon working efficiency..... 176
in the working accumulator, cause of..... 111
minimum..... 180
of the separate electrodes..... 127
Pole-potential during charging and discharging..... 106
methods of measurement..... 197
Positive accumulator plate, charged, potential against zinc..... 5
plate, formation of..... 190
plate, self-discharge of..... 137
Potential difference at the point of contact between metal and solution..... 37
difference, mercury—mercurous sulphate electrode in accumulator acid against lead peroxide and lead-sponge respectively 204
of the electrodes, effect of dilution of acid upon..... 125
Potentials of accumulator electrodes against hydrogen electrodes... 79
Precision voltmeters..... 197
Pressure, effect of, upon various galvanic elements..... 104
effect upon capacity..... 105
Prevention of separation of peroxide ions 193

Recovery, course of, calculated from *Fick's* law..... 131
from overcharging.....132, 133
of the accumulator..... 129
relation of rate to rate of discharge..... 132
Red lead, paste..... 186
v. Reichenbach, translation of monograph of *Gladstone* and *Tribe*... 2

PAGE
Relation between change of free energy of a reaction, its temperature coefficient, and heat effect 58
between vapor pressure of the acid and the E.M.F. 61
of rate of recovery to rate of discharge 132
Relations for dilute solutions 64
Resistance, causes of variation with charge and discharge 151
effect of current strength upon 148
internal, measurement of 208
internal, methods of measurement in closed circuit 210
measurements of *Boccali* 150
measurements of *Haeberlein* 150
of galvanometers and voltmeters 197, 198
variation during charge and discharge 149
Rest, during *Planté* formation 192
Reversibility of the accumulator 119
Reversible electrodes 202
galvanic combinations of accumulator and hydrogen electrodes 76
Robertson, analysis of active mass 8
Rose, see *Kohlrausch* 47, 72
Rule of *Thomson* 27

Schenek, acid density for maximum capacity 171
Schoenherr, see *Elbs* 19
Schoop, measurements of the effect of gelatinizing the acid upon working efficiency 180
Schroeder, equation for rapid-discharge capacity 157
Secondary heat of accumulator 33, 34
Seifert, test of energy-loss equation 182
Self-discharge 133
by diffusion 139
by hydrogen 139
by oxidizable impurities 138
by oxygen 139
causes of 134
of positive plate 137
rate of, influence of acid density 139
Separation of peroxide ions, prevention of 193
Sinstedten, formation of lead peroxide and lead-sponge 5
Size of element for a given taxation, calculation of 167

PAGE
Slide contact, mercury 214
Smith, see *Ayrton* 6, 7
Sodium acetate, to increase solubility of lead sulphate 189
use in negative-plate formation 189
Sodium bisulphate. 185, 186
Sodium plumbite, ionization of 44
Solubility of lead chloride in hydrochloric acid 143
of lead sulphate 71
of lead sulphate in sulphuric acid 144
Solution tension 38
Spontaneous discharge by easily oxidized impurities 138
by metallic impurities. 136
Stark, migration numbers for sulphuric acid 91
Strasser, see *Liebenow* 44
Strecker, E.M.F. of positive plate against zinc 6
Streintz, avoiding influence of *Joule* heat 33
black superoxyhydrate 6
effect of concentration of lead sulphate on E.M.F. 114
E.M.F of lead oxides against zinc 5
explanation of measurements of accumulator electrodes against zinc 80
heat value of action of sulphuric acid on lead peroxide and lead. 27
influence of acid density on E.M.F. 53
maximum temperature influence upon voltage 97
measurements of the potentials of the single electrodes 126
measurement of the temperature coefficient of the accumulator. 62
potential difference of accumulator electrodes against zinc in concentrated zinc sulphate 75
see *Tscheltzow* 12
temperature coefficient of the accumulator 93, 94
Strength of current, influence on capacity 155
Sulphate, formation at electrodes 7
formation of 11, 12
neutral, as formation electrolyte 188
Sulphate-theory 2
Sulphates of sodium, potassium, magnesium, aluminium, as formation electrolytes 188
Sulphatization 140

PAGE
Sulphatization, effect upon, of acid density 143
explanation of, by *Elbs* 141
minimum of 145
Sulphuric acid, consumption of, change in density 9
density after charging 10
dilute, electrolysis of 15
effect on solubility of lead sulphate 144
formation and decomposition of 7
heat of dilution of 29
migration number of 84
reduction of 15
table of densities, etc 219
usual density used in accumulators 20
Sulphurous acid, use in *Planté* formation 195
Superoxyhydrate, black 6

Taxation and size of element, calculation of 167
capacity for definite 156
Temperature-coefficient 93
as dependent upon acid concentration 97
calculated from secondary heats 99
equations for 95, 96
Temperature, influence upon capacity 172
Tetravalent ions of lead 42
Theory of capacity curve 161
of current origin, thermodynamical 25
of *Elbs* 21
of *Le Blanc* 39
of *Liebenow* 42
of maximum capacity 171
of origin of current, chemical 1
of origin of current, osmotic 36
of *Planté* 1
Thermic changes in the accumulator 98
effect of accumulator reaction 29
Thermodynamical calculations of ΔE 55
explanation for variation of E.M.F. with acid density 55
theory of origin of current 25
Thermodynamics, second law 25

PAGE
Thermoelement, out of accumulator 99
Thickness of plate, influence upon capacity 168
Thomsen J., heat of dilution of sulphuric acid 57
Thomson's rule 27
Tribe, see *Gladstone* 2, 7, 137, 192
Tscheltzow, E.M.F. from heat of reaction 12
heat value of action of sulphuric acid on lead peroxide and lead 27

Uppenborn, internal resistance in closed circuit 210, 212, 213

van't Hoff's equation for the relation between E.M.F. and chemical equilibrium 70
Vapor pressure of sulphuric acid solutions 61
Variation of electrode potential with acid concentration 75
of E.M.F. with acid concentration 52
of resistance during charge and discharge, cause of 149, 151
Voller, test of energy-loss equation 182
Voltage, cadmium—lead peroxide 202
cadmium—lead-sponge 202
curve, for change in direction of current 120
difference between charging and discharging with varying current strength 121
zinc—lead peroxide 202
zinc—lead-sponge 202
Voltages necessary for production of hydrogen bubbles on metals, as measured against hydrogen electrode 135
Voltmeters, precision 197
Volume, change of, during charging and discharging 103
von Ende, solubility of lead chloride in hydrochloric acid 143
von Knorre, self-discharge by manganese salts 138
von Reichenbach, translation of monograph of *Gladstone* and *Tribe*. 2

Wallentin, translation of *Planté's* "Recherches sur l'Électricité" .. 1
Water, formation of 13
Weston normal element, E.M.F. of 66
Wire, constantane 198
Wire-strand inductorium, *Nernst* 215
"Wirkungsgrad" 174
Working efficiency 174

PAGE
Working efficiency, measurement of..... 206
ratio of surfaces..... 176
Work of dissolving one gram-equivalent of a metal..... 37
Work of distillation..... 59
Work performed by external pressure in production of current..... 102

Zinc, amalgamated, as auxiliary electrode..... 201
electrode, voltage against lead peroxide..... 202
electrode, voltage against lead-sponge..... 202

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